Response to reviewer comments: "Temporal and spatial analysis of ozone concentrations in Europe based on time scale decomposition and a multi-clustering approach"

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Response to reviewer 1

Boleti et al. have used a time series decomposition methodology introduced in their previous papers to extract the long-term, seasonal and short-term components of ozone time series at around 300 measurement sites in Europe. Then they have applied a clustering algorithm separately on the long-term and seasonal components to get a two-dimensional classification of sites, according to the site type (proximity to emission sources) and to the regional characteristics (meteorological influence). Through the combination of such techniques they have gone a step forward compared to previous analyses that resulted in regional site (Carro-Calvo et al., 2017) or site type (Lyapina et al., 2016) classifications. In addition, grouping the sites according to the two categories as done here simplifies the interpretation of long-term ozone trends. The manuscript also includes some other powerful analyses, such as the application of a meteorological adjustment technique which has allowed to obtain significantly negative trends of summer peak ozone concentrations at many more sites than in previous trend assessments (e.g. Fleming et al, 2018). Furthermore, through the examination of the seasonal component they document the distinct behavior of some clusters (e.g. maximum ozone occurring earlier in the year over northern Europe than over the Po Valley) as well as a reduction of the amplitude of such cycles and a shift of the day with ozone maximum. The manuscript represents a substantial contribution to the field and considers related work by including appropriate references. I indeed find it very appropriate for publication in Atmos. Chem. Phys, but at the same time think it should substantially be improved. I have three major concerns. Two of them are related to (i) the choice of daily O3 (instead of MDA8 O3) for the main analyses presented in the manuscript, which has not been justified by the authors, and to (ii) the disconnection between the main text and large parts of the supplementary material (see main comments). My third concern is that the authors should spend time on improving some parts of the manuscript, as seen from the large number of comments included below. I think the manuscript contains a considerable number of inaccuracies, but will fully support the publication once the authors have addressed these comments.

Main Comments

1. The authors address the spatiotemporal variability of daily mean O3 in the main text and leave MDA8 O3 for the supplement. In particular, it is a bit surprising that the daily mean concentrations during the extended summer season are used in section

4.3 (Trends of peak O3 concentrations). Wouldn't it have been more appropriate to use MDA8 O3 at least for that section to focus on the times of the day with the highest ozone concentrations? I am not against this choice, but think that the authors should at least justify it. Are they using daily O3 because that simplifies the comparison of most of their results with those of other studies? If that was the case, I would understand that they have preferred sticking to daily O3 in all sections of the main text, just for consistency. Or is there any other reason?

This is true, the reason we use daily mean O3 in all sections is to be consistent throughout the manuscript and be able to compare within the paper. On the other hand, the clusters based on O3 daily mean and MDA8 are rather similar, thus, the choice of clusters between the two metrics does not affect the conclusions. As the referee mentions here, it is appropriate to use the same clusters throughout the paper, in order to compare and discuss the results. It was shown in the section 4.1 of the manuscript that the O3 daily mean depicts the main influencing factors for O3 trends, proximity to emission sources and meteorological conditions, therefore, it is appropriate to study different trend metrics based on the O3 daily mean clusters. We added the following sentences to clarify this issue in the manuscript: "The clusters based on daily mean and MDA8 O_3 are similar and the choice of clusters based on these two metrics does not affect the conclusions. The daily mean O_3 clusters depict the main influencing factors for O_3 trends, i.e. proximity to emission sources of precursors and meteorological conditions."

2. Overall, the main text and the supplement look like two completely separated pieces of work which are not properly linked. The Supplementary Material includes 5 sections and 16 additional Figures, but most of them are neither explained nor referred to from the main text. This is very unpleasant for the reader, who has to look for the appropriate sections and figures in the supplement. Bottom line: the authors should explicitly mention which section/figure of the supplement they are referring to; at the same time, they should not include analyses in the supplement if they do not refer to them from the main text.

Here are just some examples: Lines 8-11 of page 6: "In addition, a Silhouette width (Sw) analysis is performed to assess the goodness of the clustering (Rousseeuw, 1987). More details about the number of clusters, the goodness of the clustering and the Sw are provided in the supplementary material". Need to refer to some specific sections? Maybe S1-S2?

Lines 5-6 of page 8: "Here, we present the results of the daily mean LT(t)- and S(t)-clustering; results for the W(t)-clustering and the cluster analysis based on the MDA8 are provided in the supplementary material". Which sections and/or figures of the supplement you are referring to?

Line 19 of page 9: "The LT(t) signal as derived from the daily mean and MDA8 O3 observations increases" could be changed to The "LT(t) signal as derived from the daily mean (Fig. 3) and MDA8 O3 (Fig. S9) observations increases".

The results from Sections S3 and S4 (clusters and trends for MDA8 O3) are not very useful for the reader because there are hardly any specific comments about them in the main text. For instance, are the trends of daily O3 (main text) and MDA8 O3 (supplement) similar? Are the clusters of their L(t), S(t) and W(t) components overall consistent? The authors have two options: either linking the supplement and the main text much better than done now or removing many things from the supplement (e.g. focus only on daily O3 or on MDA8 O3, see previous main comment). I simply think that so much information without some proper explanations in the main text distracts the reader.

That is true, some sections in the supplementary are not clearly linked to the main manuscript. We corrected the points indicated by the referee, by referring to the corresponding section of the supplementary material where is needed in the manuscript : Lines 8-11 of page 6: "In addition, a Silhouette width (Sw) analysis is performed to assess the goodness of the clustering (Rousseeuw, 1987). More details about the number of clusters, the goodness of the clustering and the Sw are provided in the supplementary material (Sections S1 and S2)". Lines 5-6 of page 8: "Here, we present the results of the daily mean LT(t)- and S(t)-clustering; results for the W(t)-25clustering and the cluster analysis based on the MDA8 are provided in the supplementary material (Section S3)". Line 19 of page 9: "The LT(t) signal as derived from the daily mean and MDA8 O3 observations increases" has now changed to The "LT(t) signal as derived from the daily mean (Fig. 3) and MDA8 O3 (Fig. S9) observations increases". Sections S3 and S4 are now mentioned in the text, so that the reader can refer to the corresponding sections of the supplementary material.

Specific comments

1. There are some parts of Section 3 (Methodology) which need further explanations:

1.1. Additional details on the time scale decomposition should be given. For instance, the text around lines 13-15 of page 5 is not very complete: "By adding together the IMFs with frequencies between around 40 days and 3 years we obtain the seasonal variation of O3 (S(t) = c7 + ... + c10) and by adding the frequencies that are smaller than 40 days the short-term variation is acquired (W (t) = c1 + ... + c6)". First of all, according to Eq (2), the IMFs (Ci) are time dependent. So I believe it should be "S(t) = c7 (t) + ... + c10 (t)" and "W (t) = c1(t) + ... + c6(t)". The authors should explain where this decomposition (e.g. c7 to c10) and the corresponding time scales (e.g. 40 days to 3 years) come from. If this comes from the previous analyses by Boleti et al (2018) they should explicitly state that.

Indeed, the discussion on the choice of the IMFs for the seasonal and short term variations is in the publication by Boleti et al. (2018). This is now made more clear in the manuscript with the following sentence, as an extended explanation on this approach is not in the scope of this study. "A more detailed discussion on the choice of the IMFs for the seasonal and short term variations can be found in Boleti et al. (2018). " The equation for S(t) has been also corrected.

1.2. The description of the partitioning around medoids (PAM) clustering algorithm used in this study is hard to understand. For instance, around line 21 of page 5: "PAM is more robust than k-means, because it minimizes the sum of dissimilarities instead of the sum of squared euclidean distances. . . Initially, k clusters are generated randomly and the empirical means mk of the euclidean distance between their data points are calculated." First the authors say that PAM does not minimize the sum of squared Euclidean distances but then they mention "euclidean distance" when they refer to mk. I do not get it. By the way, I think it should be "Euclidean" instead of "euclidean". Around lines 3-4 of page 6: "To identify the optimal number of clusters the k-means algorithm is iteratively executed for a range of k values . . .". Now, you are referring to k-means instead of to PAM. Can you please explain all this better? From the present text it is not easy to understand what is different in k-means and PAM.

The main difference between k-means and PAM is that k-means uses centroids, while PAM uses the medoids, but they both use the Euclidean distance as a measure of difference between the data points. Indeed, this was not clear enough in the manuscript. We changed the text to the following statement: "PAM is more robust than k-means and less sensitive to outliers, because it uses medoids instead of centroids ."

1.3. Meteorological adjustment (Section 3.4). The authors use GAMS models to fit ozone on a number of variables (eq. 6). Then they follow Barmpadimos et al (2011) to calculate meteo-adjusted ozone as a function of the temporal trend and the residual from the models (eq. 7). Can you please briefly mention how the variable selection is done? Using step-wise regression like in Barmpadimos' work? And what is the overall performance of the meteo adjustement? Similar to that found by previous papers by the same authors for Swiss sites?

Variable selection was not performed in this study, but the meteorological variables used here are the ones found by Boleti et al (2019) to be the most important for O3 maximum concentrations. Nevertheless, we have now improved the manuscript to make this point more clear to the reader with the following statement: "The above explanatory meteorological variables are the ones that were most often selected in the Swiss sites by the meteorological variable selection performed by Boleti et al. (2019)."

2. The authors should provide further details about the choice, importance and characteristics of the Po Valley cluster (derived from the seasonal component of daily O3, see e.g. Figure 4). Some questions:

2.1. According to that figure and Table 1, the cluster only includes 4 sites. This is too little compared to the other clusters and therefore needs some justification. Would have this cluster appeared if the authors had kept only k=4 instead of k=5 clusters? Even if that was not the case, I understand that it might be appropriate to retain this cluster if the characteristics of this region are very different from those in the surroundings (e.g. elevated emissions and confinement of pollution within a basin with little ventilation, distinct annual cycle as seen from Figure 5).

During our exploratory analysis, in the case of k=4 clusters the sites in the Po Valley appeared together with stations in Southern France and Central and East Spain. We believe that in order to be able to study the special circumstances in this area, it is important to retain these stations in a separate cluster. We must note, that the Po Valley cluster due its small number of sites, is of course not considered a general case, but, findings in Po Valley apply only for these specific sites and area.

2.2. around line 29 of page 9: "The sites in "PoValley" display the most pronounced S(t), mainly due to the Mediterranean weather conditions, e.g. high temperatures. At the same time high NOx and VOC emissions in this region leads to higher O3 concentrations". I am not convinced at all with this statement. Note that the amplitude of the S(t) component is remarkably wider both for the Po Valley and the Central North cluster compared to the others (Figure 4). I am surprised at the results for the Central North cluster, where I would expect average ozone concentrations during the warm season (but not in the colder months) to be clearly below those in the Po valley. The authors should explicitly mention this similarity between two apparently very different regions and, if possible, explain why this happens. In other words, are there any reasons why the impact of meteorology and emissions on ozone presents stronger seasonality in these two regions than in others? In addition, I would remove "Mediterranean weather conditions, e.g. high temperatures", which I find quite vague. I think the expression "Mediterranean weather conditions" is much more appropriate for the coastal sites in Spain, southeastern France and in the proximity of Rome (see Figure 1). I am not sure that "e.g. high temperatures" is appropriate either here because this analysis includes ozone data in all seasons.

The Central North high seasonal values are probably related to the industrial and agricultural emissions, and is now mentioned in the manuscript as follows: "It is interesting to note that both Central North sites have seasonal values in their signal comparable to the Po Valley values, probably related to industrial and agricultural emissions in the area of Northern Germany." Higher temperatures in Po Valley compared to rest Central and Northern Europe in combination with the high emissions and topographic conditions (valley south of Alps) that trap the emitted pollutants and retain cyclonic systems in the area lead to the observed high concentrations. To make this more clear we added the following statement: "Special topographic conditions (valley south of Alps) contain emissions from the Milan industrial area in combination with cyclonic systems (Bärtsch-Ritter et al., 2004; Henne et al., 2005; Thunis et al., 2009; Prévôt et al., 1997)."

3. In the long paragraph between lines 4-21 of page 10 the authors compare the results to those of previous classifications, namely Carro-Calvo et al. (2017) and Lyapina et al. (2016). See comments:

3.1. The comparison of the results of the S(t) clustering to those by Carro-Calvo is probably too exhaustive. I would simplify it, but this is up to the authors to decide whether they want to do that. Rather than mentioning every single regional difference arising from the comparison of both classifications, I would instead list all the possible reasons why the results of both classifications are expected to differ. Only some of those reasons are mentioned in the text. Basically, Carro-Calvo used a MDA8 O3 gridded dataset considering only the summer months, while daily O3 at specific sites during the whole year is used here. In addition, Carro-Calvo applied k-means on normalized anomalies while the spatial classification presented here is based on the seasonal component. Finally, the authors are right to indicate that some of the clusters of Carro-Calvo et al. (2017) do not appear here because the former study used gridded data over locations with few observations, but this explanation is not complete. Note that the final number of clusters will depend on the a-priori choices made (e.g. decisions on the number of clusters based on the explained variance achieved, intra-cluster variance or RMSE, minimizing correlations among different clusters, silhouette width, and so on).

Indeed, the comparison would suffice by explaining the reasons of the differences between both studies. The respective part of the manuscript is now as follows: "Compared to Carro-Calvo et al. (2017), similar geographical clusters were identified here, except for the Iberian Peninsula, eastern Europe, northern Scandinavia and the Balkan states that do not appear as separate clusters in our analysis. This is most probably due to the small number of observational sites in the above regions. In contrast to our study, gridded MDA8 O_3 concentration during summer have exclusively been used for the cluster analysis by Carro-Calvo et al. (2017), therefore conditions when the correlation of O_3 and meteorological variables such as temperature is typically strongest. In addition, the present study results in spatial classification by utilizing the seasonal variation, while Carro-Calvo et al. (2017) have used normalized anomalies." It is true that number of clusters depend on a-priori choices. We believe that in addition to the above argument, the reason for this difference here is that our data set completely lacks data points in the regions of eastern Europe, northern Scandinavia and the Balkan states.

3.2. I feel the comparison of the results from the L(t) clustering to those of Lyapina et al. (2016) would benefit from some additional explanations. That work performed two cluster analyses (CA). The first CA used absolute mixing ratio values and resulted in 5 clusters (Table 2 of that paper), while the second CA used normalized mixing ratios and yielded 4 clusters (Table 3 of that paper). As it is not straightforward to summarize the description of the clusters in those tables, one could just select one of them (e.g. the first one) and provide some simple explanations. For instance, one could indicate that the results from this study are similar to those of a classification by Lyapina et al. (2016) who found 5 clusters of different type, ranging from urban traffic (equivalent to the "highly polluted" reported here) to rural background.

Indeed, it is useful to strengthen this comparison. We changed this part to the following sentence: "Four site type clusters were found based on the LT(t) in this study similar to Lyapina et al. (2016) based on absolute mixing ratios of O_3 variations, which identified five site type clusters ranging from urban traffic (as the "HIG" cluster here) to rural background environments (equivalent to "RUR"). "

3.3. It is very good that the authors have acknowledged previous work and compared their results to those studies. Apart from that, either here or somewhere else in the paper, I would emphasize the strength of this work: they authors have clearly gone a step forward compared to those studies because they have provided a two-dimensional classification.

We have updated part of the Conclusions section with two additional sentences. "Such a two-dimensional site classification scheme provides an poweful approach for O_3 trends studies in large spatial domains and can be of significant use in model evaluation studies (e.g. Otero et al., 2018)."

4. Figure 5 (Annual cycle of daily mean O3 S(t) for the daily mean S(t) clusters) appears on page 12, but I think it is not referenced to from the main text. The figure should be moved to another part of the text (Section 4.4. Ozone seasonal cycles), which would affect the numbering of other figures. Then, in section 4.4, it would be good to mention some of the main features seen from the S(t) component of daily O3 in that figure. For instance, the figure nicely shows that the ozone maxima occurs in summer for the Po Valley cluster and much earlier in the year in the North cluster. This is consistent with previous studies that have reported that both the highest average ozone concentrations and extreme ozone episodes tend to occur over central/southern Europe during summer and over northern Europe in spring (see e.g. Figs 1 of both Schnell et

al., 2015 and Ordonez et al., 2017). Finally, I would explicitly mention the days of the ozone maxima in each cluster when commenting the trend of DoMax in Table 2.

This is right, the figure with the annual cycles fits better to section 4.4 and shows more explicitly the differences in annual cycles across the different parts of Europe. We added the following sentences in the manuscript: "In Fig. 8 the average annual O_3 cycles are shown; it is clear that in Po Valley the day of maximum O_3 occurs in summer (June-July), while in the North occurs around spring time (late March-April). This agrees with previous studies, where both the highest average O_3 concentrations and extreme O_3 episodes tend to occur over the central and southern parts of Europe during summer while over northern Europe during spring (Schnell et al., 2015; Ordóñez et al., 2017)."

5. Section 4.2 is on trends of daily mean ozone, but Figure 7 at the end of that section shows results of MDA8 LT for Mace Head. Why do you use MDA8 instead of daily O3 for that particular figure? Is it just to compare the results with those of Derwent's papers (see first paragraph of page 14)?

Indeed, the reason for the choice of the MDA8 in this case is a direct comparison to study by Derwent et al (2013). We now clarify this as follows: " .. we estimated the LT(t) variation of MDA8 O_3 and the Theil-Sen trend for the site in Mace Head (Fig.7) to compare with the MDA8 O_3 trend identified by Derwent et al. (2018)"

6. As seen from the first paragraph of section 4.3 (trends of peak O3) the main result from that section is that, unlike previous studies like that of Flemming et al. (2018), the meteorological adjustment results in significantly negative trends at many sites. That is a very nice result, but I am not fully convinced with all the interpretations of the trends in the following paragraph. For instance, around lines 17-20 of page 14: "in the "BAC" cluster (especially the "West" cluster) the decrease of MTDM was not so pronounced, likely due to the increase of hemispheric transport of O3 in Europe (Derwent et al., 2007; Vingarzan, 2004)". However, those papers roughly cover the first halve of the period of analysis, where I agree that might have been the case (see e.g. Figure 7 for a different metric at Mace Head). Moreover, a few lines below (lines 1-3 of page 15) they claim that there might be some connection between the industrialization of Eastern Europe and the trends in some clusters (lines 1-3 of page 15). I admit that these interpretations are plausible and that the authors have been reasonably careful with their statements, but I would add a short sentence to mention that some more dedicated analyses (e.g. modelling studies) would be needed to investigate the reasons for such trends. I fully understand that such analyses are out of the scope of this paper.

The referee is correct, in order to know exactly the source of such behavior, modeling studies are needed. To make it clear we added in the manuscript the following statement: "Nevertheless, in order to estimate the reasons and quantify the exact influence of the above factors on the trends, dedicated modelling studies are needed."

7. I also like the idea of examining the seasonal cycles of O3 in Section 4.4 and the results presented there are relevant. However, I am not convinced about some of the explanations given there as there are some inaccuracies. In addition, I am not happy at all with the writing and believe that this section has been written in a rush. There are so many inaccuracies and corrections to make (some of them included in the technical corrections section) that it very hard to focus on the science. Examples: *

Lines 17-19 of page 16: "The increase in the Smin(t) may be partially due to the . . .and probably due to the increased influx of O3 towards north and northwest Europe and more cyclonic activity in the North Atlantic during winter as well (Pausata et al., 2012)". Apart from improving the writing (too many "ands" within the same sentence), I am not convinced at the explanations regarding Pausata's paper. What you do mean by increased influx and cyclonic activity? Are such things really mentioned that way in that paper? If so please explain this better. As far as I remember, that work simply suggested that the increasing baseline ozone in western and northern Europe during the 1990s could be associated with a prevailing NAO+ phase during that period.

In winter, positive NAO conditions are linked to enhanced westerly flow as well as intercontinental transport of air masses. Thus, the increase of winter O3 values (Smin(t)) might be linked to the increase of baseline O3 that Pausata et al. (2012) have found in their study, which is related to the positive NAOI. We rephrased our statement as follows and improved the readability as follows: "An increase in baseline O_3 related to the prevailing positive NAO Index -and the associated westerly flow and intercontinental transport- during 1990s and beginning of 2000s is probably a factor contributing to the increase of the winter Smin(t) O3 values."

* Lines 24-27 of page 16: "The observed shift of the day of seasonal maximum might be linked to the increase of emissions in East Asia that have contributed to increased transport of air pollution to middle-and northern latitudes (Zhang et al., 2016) where the effect on O3 is probably greater due to greater convection, reaction rates and NOx sensitivity [some refs.]. . .". Need to completely rewrite this sentence because it is hard to understand. I assume that the strong convection takes place in East/Southeast Asia instead of at mid/north latitudes as it reads now from this sentence. In addition, the word "greater" is repeated within the same line.

We have rewritten this sentence as follows: "The observed shift of the day of seasonal maximum might be linked to the increase of emissions in East Asia. The associated strong photochemical reaction rates, convection and NO_x sensitivity in the tropics and subtropics (Derwent et al., 2008; West et al., 2009; Fry et al., 2012; Gupta and Cicerone, 1998) have probably contributed to increased transport of air pollution to middle and northern latitudes (Zhang et al., 2016)."

* Line 31-33: "The positive phase of the NAO leads to increased O3 concentrations in Europe through higher westerly winds across the North Atlantic, and enhanced transport of air pollutants from North America to Europe (Creilson et al., 2003)." All this looks a bit redundant. Do you simply mean that "The positive phase of the NAO leads to increased O3 concentrations in Europe through enhanced transport of ozone and precursors across the North Atlantic from North America to Europe (Creilson et al.,2003)"?

That is right, we updated this sentence: "The positive phase of the NAO leads to increased O_3 concentrations in Europe through enhanced transport of O_3 and precursors across the North Atlantic from North America to Europe Creilson et al. (2003)."

Technical comments and corrections

- Line 3 of page 1 (abstract): "the effect of these reductions on ozone is investigated by analyzing surface measurements of ozone". Change the second "ozone" to "this pollutant" just to avoid redundancies.

  Done.

- Lines 13-14 of page 1: "The effect of hemispheric transport of ozone can be seen either in regions affected by synoptic patterns in the northern Atlantic or at sites located at remote high altitude locations". I do not consider this as an appropriate sentence for the abstract. The manuscript includes some references on the impact of long-range transport and changing weather patterns (e.g. impact of the NAO), but it does not provide any supportive evidence of the relevance of such processes.

  That is true, we excluded this sentence from the abstract.

- Lines 17-18 of page 1: "while seasonal cycle trends and changes in the sensitivity of ozone to temperature are driven by regional climatic conditions". I would tone down this statement. Honestly, I do not think that the manuscript proves that this impact is larger than that of the varying rates of ozone precursor emission reductions over the different regions.

  To make it more clear that the climatic factors are indeed influencing the trends but are not the only factors that play a role in the observed trends we changed this statement to the following: "while seasonal cycle trends and changes in the sensitivity of O_3 to temperature are among other factors driven by regional climatic conditions."

- Last line of page 2 (Introduction): "For instance, in the U.S., O3 climate penalty – defined as the slope of the O3 versus temperature relationship – dropped from 3.2 ppbv/C before 2002 to 2.2 ppbv/C after 2002 as a result of NOx emission reductions (Bloomer et al., 2009)". One could add a reference to Colette et al. (2015), who analysed chemistry-transport and climate-chemistry model projections to asses the impact of climate change on this climate penalty over Europe by the turn of the century.

  This is right, we added the following sentence: "Additionally, Colette et al (2015), based on chemistry-transport and climate-chemistry model projections, assessed the impact of climate change on the climate penalty and found that over European land surfaces summer O_3 change is [0.44; 0.64] and [0.99; 1.50]ppbv (95% confidence interval) for the 2041-2070 and 2071-2100 time periods, respectively."

- First line of page 4: "during May and September" -> between May and September

  Done.

- 5th line of page 4: Did you use surface pressure or sea level pressure (SLP)?

  We used surface pressure.

- Line 21 of page 5: Move "e.g." to the beginning in "(Lyapina et al., 2016, e.g.)".

  Done.

- Line 17 of page 6: where yd (t) the de-seasonalized -> where yd (t) is the de-seasonalized

Done.

- Line 19 of page 6: "of the" can be removed from "de-seasonalized concentrations of the yd (t)".

Done.

- Line 25 of page 6: "because" is repeated within the same sentence.

The sentence is now improved to the following: "A different approach for meteorological adjustment was used for the peak O_3 than for the daily mean and MDA8; de-seasonalization is not meaningful for peak O_3 because peak O_3 events are temporally localized."

- Lines 4-5 of page 7: "For the GAMs, the following meteorological variables were used". I would remove "meteorological". Reason: the Julian day, which is not a meteorological variable, is also included in the model.

We corrected this, by specifying that the Julian day is a time variable. "For the GAMs, the following meteorological variables were used: the daily maximum temperature, daily mean specific humidity, daily mean surface pressure, daily maximum boundary layer height, morning mean convective available potential energy (CAPE), daily mean East-West surface stress and daily mean North-South surface stress, as well as a time variable the Julian day."

- Line 6 of page 7: Again "daily mean surface pressure". Do you mean SLP?

Surface pressure was used in the models.

- Line 7 of page 7: No need to spell out CAPE again.

Right, this has been corrected.

- Line 8 of page 9: "mostly located at higher altitudes". Higher than what? "Higher" could be changed to something like "relatively high" or "elevated".

We changed to "relatively high altitudes".

- Lines 9-10 of page 11: "the positive trends can be partly explained by . . . originating from the diesel vehicles". Change to "the positive trends could partly be explained by . . . originating from the proliferation of diesel vehicles"

Done.

- Line 6 of page 12: "rural sites and small and non-significant" -> "rural sites as well as small and non-significant"

Done.

- Figure 6: Please indicate what the box-plots indicate (i.e. median, edges of the boxes: 25-27th percentiles, whiskers related to interquartile range or to some specific percentiles, etc.).

We clarify this by adding the following sentence. "Boxes include 25th to 75th percentiles with the line indicating the median value; whiskers extend to 1.5 times the interquartile range."

- Lines 7-8 of page 13: "Trends were estimated 0.08 ppb/year [0.06,0.1] for the first period and -0.04 ppb/year [-0.09,0.02] for the second period". Lines 1-2 of page 14: "Derwent et al. (2018) have found an increase of 0.34 $\pm$ 0.07 ppb/year with a deceleration rate after 2007 of -0.0225$\pm$ 0.008 ppb/year". If possible, indicate if the uncertainty estimates correspond to the 95% confidence intervals or to something else. There are other parts of the text where this is not clear.

  In the Methods Section 3.3 it is mentioned that the 95% confidence interval is used for the calculation of the trend.

- Section 4.2 is on the trends of daily mean ozone, but Figure 7 at the end of that section shows results of MDA8 LT for Mace Head. The results look convincing, but why do the authors use MDA8 instead of daily O3 for that particular figure? Is this just to compare the results with those of Derwent's papers (see first paragraph of page 14)?

  Yes, the MDA8 is used for direct comparison to the result by Derwent et al (2018).

- Lines 6-7 of page 14: The word "increased" can be removed from both lines.

  Done.

- Lines 1 and 5 of page 16: "central Northeast Germany" and "central Northeast region". Do you mean "central and northeast"?

  Indeed, the right expression is "central and northeast".

- Line 28 of page 16: "meteorological factors have affected" -> "meteorological factors may have affected".

  Done.

- Line 30 of page 16: Add space before while in "data,while".

  Done.

- Line 34 of page 16: "resulted to" -> "resulted in" (this should be changed somewhere in the supplement too).

  Done.

- Caption of Figure 9 on page 17: Change "pm" to "+/-" in "average pm the standard deviation".

  Done.

- Line 2 of page 17: "more increased" -> "increased"

  Done.

- Lines between pages 17 and 18: "The early spring maximum in the "North" sites in April can be explained by higher NOx that is released from PAN and . . .". What do you mean by "higher NOx"? Higher than what? Do you mean something like elevated NOx? By the way, why don't you refer to Figure 5 here (see comment above)?

"Elevated NOx" is indeed a more appropriate term. Figure 5 is now moved to this section as Figure 8 and added as a reference in this sentence.

- Table 2 on page 18: According to the methods section, one should write "SDoM". Need to change that in the caption and header of last column.

Done.

- Lines 6-9 of page 19: "At PoValley sites the decrease was more pronounced (-0.083 ppb/K/year). At the same time the average correlation between O3 and temperature is the highest compared to the other regions, because of large reductions of precursors concentrations in this region which is characterized by high industrial emissions". I assume you mean something like "At PoValley sites the decrease was more pronounced (-0.083 ppb/K/year) because of large reductions of precursor concentrations in this region which is characterized by high industrial emissions. Note that the average correlation between O3 and temperature in that cluster is the highest compared to the other regions".

Yes, that is right. We changed the sentence to the above suggestion.

- Lines 9-11 of page 19: Regarding the low correlations between O3 and T in the North cluster I would also mention the low temperature ranges observed there compared to the other clusters (Fig 11).

We already discuss this feature in the following sentence: "This is expected because at these high latitudes mean temperature is lower compared to other regions in Europe (Fig. 11), thus, photochemical production of O_3 is weak during the time when O_3 typically reaches its maximum concentration." Nevertheless, we added in the text the reference to figure 11 to highlight this difference.

- Lines 12-16 of page 19. Discussion of the stronger trends of the O3-T relationship for the more polluted LT(t) clusters: "Our results are in line with a box-model study that tested the O3-temperature relationship under different NOx level scenarios (Coates et al., 2016). Coates et al. (2016) have shown that at high NOx conditions O3 increases more strongly with temperature, while the increase is less pronounced when moving to lower NOx conditions". As mentioned for the Po Valley S(t) cluster (see a couple of comments above), I don't see a clear relationship. These references are related to the strength of the O3-T relationship but not to the trend of that relationship. I assume that you mean that regional ozone production has mainly decreased at the most polluted locations, due to considerable reductions of precursor emissions there. Need to rewrite.

Yes that is a valid argument. We have made it more clear to the reader by adding the following sentence according to the referee's comment: "Consequently, regional O_3 production has mainly decreased at the most polluted locations, due to considerable reductions of precursor emissions."

- One can remove the columns "standard deviation" in Tables 3 and 4. The p-values should suffice.

That is true, but we believe that it gives a good perspective on the range of variation in the trend magnitudes.

- In different parts of the text, the authors indicate that the S(t) clusters represent the "climatic conditions". I would add the word "regional" to clearly indicate that this is indeed a geographical classification that clearly reflects the regional climate conditions. This can be done in different parts of the text. Here I simply include an example for lines 5-6 of page 21: "Our approach captures several features of O3 variations, i.e. pollution level from the L(t)-clustering and influence of the climatic conditions from the S(t)-clustering". I would change the end of this sentence to "influence of the regional climate conditions from the S(t)-clustering".

  Indeed, "regional climate conditions" is a more accurate expression. We changed this in several parts of the manuscript.

- Lines 17-18 of page 21 (Conclusions): "peak O3 has been decreasing with the smallest rate at higher altitude sites especially in the western part of Europe due to the influence of background O3 imported from North America and East Asia". Are the evidences for this long-range-transport influence so clear? If not I would add the word "possibly" before "due to".

  That is right, the argument was not proven here. We added the word "possibly" in the statement.

- Line 24 of page 21: "the sensitivity of O3 to temperature has weakened since 2000 with a rate of around 0.084 ppb/K/year". It should be considerably less than that because that value is only found for the 4 sites in the Po Valley cluster (see Tables 3 and 4).

  True, this is a typing error. The true average value is 0.04 ppb/K/year.

- Lines 25-26 of page 21 (about the decreasing O3-T slope): "It was shown that differences in changes to this sensitivity across sites are mainly driven by regional meteorological conditions". I do not see any proof of this in the manuscript. It might well be related to varying rates of reductions of precursor emission across the different regions. I have a similar comment about this in the abstract so both of them can be addressed at the same time.

  The main argument here is that the trend differs amongst the regional clusters, thus, the climatic conditions probably influence this trend. Nevertheless, we rewrote this part to clarify this argument as follows: "Finally, the sensitivity of O_3 to temperature has weakened since 2000 with a rate of around 0.04 ppb/K/year, i.e. formation of O_3 became weaker at high temperature conditions, that can be attributed to the decrease of NO_x concentrations. The trend of the sensitivity differs across sites that are influenced by different meteorological conditions."

- The references Boleti et al. (2018a) and Boleti et al. (2018b) should be changed to Boleti et al. (2018) and Boleti et al. (2019), respectively. The second paper has been published and should be updated in the reference list.

  Done.

- Figures S1 & S2: Can you please enlarge fonts. They are too small and very hard to read.

  Done.

- Lines 2-3 of page 3 in Supplement: "objects have a low similarity with the rest objects" -> "objects have low similarity with the rest of the objects"

Done.

- Figure S3: Even when there are some explanations on the previous page, most readers are not very familiar with the concept of silhouette width. In the figure caption I would indicate (1) that each horizontal bar represents the silhouette width for a particular site in a given cluster and (2) that this parameter is clearly positive for most sites.

  We added the following in the caption: "The bars indicate the value of the S_W for a particular site within the respective cluster. For the majority of the sites the S_W is positive showing high similarity within the clusters."

- Figure S5: I assume this is for W(t) instead of for S(t).

  That is right, we corrected to W(t).

- Section S3 (Additional information on clusters): What is the use of this section if you hardly provide any comments e.g. about the MDA8 O3 clusters in the main manuscript? As indicated above, the main text and most of the supplement seem detached from each other.

  We believe that it is interesting to show that both metrics lead to similar results. Also, we have now connected this Section to the main manuscript, as described in response 2 of the main comments.

- Lines 2-4 of page 10 in supplement: "In this section we present more detailed information about the clusters extracted from the daily mean and MDA8 O3 LT(t), S(t) and W(t)". Please refer to Figures S9-S11 there.

  Done.

- Caption of Figure S9: Need to remove "Map indicating the sites that belong in each cluster and average LT(t) in each cluster with the standard deviation of the sites that have SW>0".

  Done.

- Captions of Figures S10-S12: Need to use subscript for W in "SW" (silhouette width, defined in section S2).

  Done.

- Lines 4-5 of page 14 in supplement: "The level off or small increase in the HighPoll stations can be attributed to the smaller rate of reduction of VOCs, which resulted to reduced titration of O3 by NO". I agree with the reduced titration due to the decrease of NOx emissions, but do you have any evidence about the smaller rate of reduction of VOCs? If so one should provide a reference. A simpler explanation might be a change of chemical regimes, i.e. in the sensitivity of O3 production to NOx and VOCs.

  The smaller reduction rate of VOCs can be seen in the report by (EEA, 2017). This reference is now added to the text, as well as the suggested argument about the chemical regimes. "An additional explanation for the observed trend might be a change of chemical regimes , i.e. in the sensitivity of O_3 production to NO_x and VOCs."

– Line 6 of page 14 in supplement: Change "(Fig. S14" to "(Fig. S14)". Then remove "respectively" because it is not needed there.

Done.

– Lines 10-11 of page 14 in supplement: "Here, the sites with negative SW that were not considered in the discussion of the trends are presented. In the LT(t)-clustering four sites with negative SW were identified (Fig. S15), in the S(t) 26 sites (Fig. S16) and in the W(t) 24 sites". It is unclear whether you are talking about the clusters of daily O3 or MDA8 O3.

It is the daily mean O_3 clusters, we have corrected this to "daily mean O_3 LT(t)-clustering".

– Caption of Figure S15 is not complete. Need to indicate the meaning of the different lines/shading.

Done.

– Caption of Figure S16 is not complete either. For instance you don't show the "clusters average S(t)" as you claim because there is some spread in the figure. Probably mean +/- standard deviation?

Right, it is the average $\pm$ the standard deviation. The caption is now improved as follows. "Example cases of sites with negative SW in the S(t)-clustering (black dashed line) in comparison with the clusters average S(t) $\pm$ the standard deviation (shaded area)."

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Response to reviewer comments: "Temporal and spatial analysis of ozone concentrations in Europe based on time scale decomposition and a multi-clustering approach"

Eirini Boleti, Christoph Hueglin, Stuart Grange, Andre Prevot, Satoshi Takahama

Response to reviewer 2

The manuscript presented by Boleti et al. examines trends on surface ozone concentrations across a number of stations over Europe for the period 2000-2015. They use a time-scale decomposition to analyse long-term (LT), seasonal (S) and short-term (W) variations. Then, they apply a clustering technique and they finally calculate the trends in the clusters obtained. In addition, they analyse the ozone-temperature relationship over the different clusters and sub-periods. Their classification is consistent with previous studies and their results show a general decreasing in the ozone concentrations, mostly in the ozone peaks. In addition they find a reduced sensitivity in the ozone- temperature relationship over most of the clusters defined. Overall, I found the manuscript very interesting and complete. The methodology applied is robust and consistent, as well as the results presented. However, I also think that there are some parts in the current version that should be improved in order to be published, in particular the methods sections (see my comments below). In my opinion the manuscript might be a good contribution to Atmos. Chem. Phys and the scientific community. Therefore, I would be happy to support the publication of the present manuscript after addressing some comments, which I consider that would be useful to improve it. I have a few general comments and some specific comments:

Main Comments

There are some parts in the methods section that are not very clear, and in my opinion this section is essential to follow the manuscript. Therefore I have some comments and questions that I would like to ask the authors:

1. Section 3.1. Time scale decomposition (page5): The authors should explain in more detail the IMF. How the number of coefficients (c_j) is selected? The authors say "By adding together IMFs with frequencies around 40 days and 3 years we obtain the seasonal variation of O3 (c_1 +...c_{10})", but why 40 days and 3 years? Is this based on the previous study from Boleti et al.2018? I think that this information should be included in order to help the reader to better understand the methodology.

The selection is discussed in Boleti et al. (2018) and for the reader that is more interested on that matter we refer to the above publication. We have added the sentence: "A more detailed discussion on the choice of the IMFs for the seasonal and short term variations can be found in Boleti et al. (2018)."

2. Sections 3.3-3.4 Long-term trends (page 6, 7): I understand that for the peaks of O3 metrics the method explain in section 3.3 cannot be applied. But, it would possible to use the same method, i.e. GAMs models also for daily mean and MDA8 O3, wouldn't it?

Yes, that would be another good approach to estimate meteorological influence of daily mean and MDA8 O_3.

3. Why the authors define the warm season as May-September? Why April is not included? I think this should be further clarified, since usually ozone season ranges from April to September (e.g. EEA, 2019, Fleming et al. 2018)

This is based on the estimation of the MTDM which In previous reports by the EEA refers to the period between May and September. Thus, for consistency and to compare our study with the EEA studies, we keep this period of the year as representative for occurrences of peak O_3. We now mention the above in the manuscript: "The models are fitted for the warm season May-September as by definition the MTDM refers to this period of the year."

4. Reading the modelling part (section 3.3, 3.4, page 6) is not clear the input data to calculate the trends, e.g. the GAM models are fitted to each cluster that contains a number of stations, so the models are applied individually to each station, am I right?

A GAM model is applied to each station separately and the trends are calculated for the individual stations as well.

5. Regarding the analysis of seasonal cycle of O3, why do the authors chose the mean of O3 and not the MDA8 O3?

The reason we use daily mean O3 in our analysis is to be consistent throughout the manuscript and be able to make comparisons between the different O3 metrics and clusters.

Specific comments

1. L26-30 of page 3. The authors applied a filter to obtain the time series, and only those with a maximum of 15% of missing values and maximum of 120 consecutive days are used. Is this 15% applied to whole period (16 years) or each year? And the consecutive days? I assume that they refer those 120 consecutive days in one year, is that correct? Can the authors clarify this?

15% missing data and the 120 consecutive days refer to the whole period of measurements. Thus, we clarify this with the following addition: "time series with a maximum of 15% of missing values, and a maximum of 120 consecutive days with missing values are used for the whole period of measurements, leaving the study with 291 sites across the European domain."

2. L1 of page 5. I would add that the clusters are identified by using each component L(t), S(t), W(t) separately to the algorithm.

The following sentence is already mentioned in the manuscript: "For identification of the clusters the LT(t), S(t) and W(t) of the daily mean and MDA8 O_3 were used as input time series in the PAM algorithm."

3. L4 of page 8. What are the temperature ranges considered?

The temperature ranges from 7 to 35 degrees Celsius in intervals of four degrees; (7,11] (11,15] (15,19] (19,23] (23,27] (27,31] (31,35]

4. L4 of page 9. Why do the authors leave the results of MDA8O3 in the supplement and the results if the O3 in the main text? Wouldn't it be more interesting to see the results for MDA8O3?

We refer to our answer of the main comment 1 from referee 1. In summary, O3 daily mean and MDA8 clusters are rather similar, the choice of clusters between the two metrics does not affect the conclusions. In addition, for comparison with other studies and consistency throughout the manuscript, we believe it is more interesting to present the daily mean O3 clusters.

5. L19-23 of page 9. Please refer to figure 3.

Done.

6. L25 of page9. Just a comment regarding Fig.4. the colours for "Po Valley" and "Central South" maybe could be changed, they are quite similar and it is hardly to distinguish the stations that belong to each cluster.

This is a valid remark, we changed the color of the Po Valley cluster to a darker blue color.

7. L4-L20 of page 10. Should Figure 5 be referred here? I couldn't find any reference to Fig.5.

This is true, the figure is now moved to the section 4.4. O3 seasonal cycle trends, after a similar suggestion of referee 1.

8. L3 of page 11. "decreasing O3 trends", maybe it should be specified "decreasing daily O3 means".

That is right, it is corrected to "decreasing daily O3 means".

9. L4 of page 11. In my opinion, the table 1 with the number of stations should be introduced before (e.g. when presenting the clusters).

Indeed, we have moved this table in section 4.1. Cluster analysis.

10. L9 of page 14. Where these percentages 62% and 18% came from exactly? Is there any figure to support this? This question is in the line of one my previous comment (i.e. how the models are fitted).

We do not have a figure to support this. These percentages refer to the sites, where negative trends were estimated from all studied sites in our data set, i.e. ratio: sites with negative trends/number of all sites, 62% before and 18% after meteo-adjustment.

11. L10 of page 19. In the North sites the variability of temperature is lower and O3 is also more influenced by transport.

This is indeed a useful addition to the manuscript. "In addition, in these northern regions the variability of temperature is lower compared to the central and southern parts of Europe, while O_3 concentrations are more influenced by intercontinental transport mechanisms."

12. L24-26 of page 21. The authors attributed the decreasing O3-Temperature to NOx reductions, and this is likely one of reasons (but it is not showing here) and then, they mention that "changes in the sensitivity across sites are mainly driven by regional meteorological conditions", so what about the NOx emission reductions just mentioned? I think this last paragraph is important and it must be rewritten.

We rewrote this paragraph to the following one: "Finally, the sensitivity of O_3 to temperature has weakened since 2000 with a rate of around 0.04 ppb/K/year, i.e. formation of O_3 became weaker at high temperature conditions, that can be attributed to the decrease of NO_x concentrations. It was shown that the trend of the sensitivity differs across sites that are influenced by different meteorological conditions."

References

Boleti, E., Hueglin, C., Takahama, S., 2018. Ozone time scale decomposition and trend assessment from surface observations in switzerland. Atmospheric Environment 191, 440–451.

Temporal and spatial analysis of ozone concentrations in Europe based on time scale decomposition and a multi-clustering approach

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Abstract.

Air quality measures that were implemented in Europe in the 1990s resulted in reductions of ozone precursors concentrations. In this study, the effect of these reductions on ozone is investigated by analyzing surface measurements of ~~ozone~~ this pollutant for the time period between 2000 and 2015. Using a non-parametric time scale decomposition methodology, the long-term, seasonal and short-term variation of ozone observations were extracted. A clustering algorithm was applied to the different time scale variations, leading to a classification of sites across Europe based on the temporal characteristics of ozone. The clustering based on the long-term variation resulted in a site type classification, while a regional classification was obtained based on the seasonal and short-term variations. Long-term trends of de-seasonalized mean and meteo-adjusted peak ozone concentrations were calculated across large parts of Europe for the time period 2000-2015. A multi-dimensional scheme was used for a detailed trend analysis, based on the identified clusters, which reflect precursor emissions and meteorological influence either on the inter-annual or the short-term time scale. Decreasing mean ozone concentrations at rural sites and increasing or stabilizing at urban sites were observed. At the same time downward trends for peak ozone concentrations were detected for all site types. ~~The effect of hemispheric transport of ozone can be seen either in regions affected by synoptic patterns in the northern Atlantic or at sites located at remote high altitude locations.~~ In addition, a reduction of the amplitude in the seasonal cycle of ozone was observed, and a shift in the occurrence of the seasonal maximum towards earlier time of the year. Finally, a reduced sensitivity of ozone to temperature was identified. It was concluded that long-term trends of mean and peak ozone concentrations are mostly controlled by precursors emissions changes, while seasonal cycle trends and changes in the sensitivity of ozone to temperature are among other factors driven by regional climatic conditions.

1 Introduction

Tropospheric ozone (O_3), together with particulate matter and nitrogen dioxide (NO_2), is one of the most troublesome air pollutants in Europe (EEA, 2016). 17,000 premature deaths every year are attributed to excess O_3 exposure, without any sign of reduction in number of fatalities (EEA, 2016). In terms of impact on ecosystems, elevated concentrations of tropospheric O_3 are responsible for damaging agricultural production and forests mainly by reducing their growth rate. In addition, tropospheric

O_3 acts as a greenhouse gas with an estimated globally averaged radiative forcing of $0.4 \pm 0.2\,W/m^2$ (IPCC, 2013). In the 1990s emission control measures on O_3 precursors, namely nitrogen oxides (NO_x=NO+NO_2) and volatile organic compounds (VOCs), were implemented in order to regulate air pollution. As a result, concentrations of NO_x and VOCs have significantly declined in Europe (EEA, 2017; Colette et al., 2011; Guerreiro et al., 2014; Henschel et al., 2015). Especially, NO_x emissions declined in Europe by 48% between 1990 and 2015 (EEA, 2017).

Surprisingly, O_3 concentrations have not decreased as was expected (Oltmans et al., 2013; Colette et al., 2018). Mean O_3 concentrations have either remained stable or even increased in rural, background areas from 1990s and until mid-2000s in many European countries (Boleti et al., 2018; Munir et al., 2013; Paoletti et al., 2014; Querol et al., 2016; Anttila and Tuovinen, 2009, e.g.). At urban sites an increase of mean O_3 has been observed; in some cases, an increase has been found at both rural and urban sites with larger upward trends observed at urban compared to the rural sites (Paoletti et al., 2014; Querol et al., 2016; Anttila and Tuovinen, 2009). However, a change in the trend has been observed after mid-2000s, when mean O_3 concentrations have started to decline (Boleti et al., 2018; Munir et al., 2013). On the other hand, maximum O_3 concentrations decreased continuously from the 1990s until present (Paoletti et al., 2014), except for the traffic loaded environments (Boleti et al., 2019). Downward trends of different metrics for peak O_3 have been found at many sites across Europe (Fleming et al., 2018). However, the high year to year variability of O_3 tends to mask the long-term changes leading to a large fraction of sites with non-significant trends . Several studies based on either observations or climate models have shown that anthropogenic emissions can affect O_3 concentrations across continents (Dentener et al., 2010; Wild and Akimoto, 2001; Lin et al., 2017). The increase of background O_3 in Europe has been associated with increasing stratospheric O_3 contribution (Ordóñez et al., 2007), as well as increased hemispheric transport of O_3 and its precursors.

A shift in the seasonal cycle of O_3 has been observed in northern mid-latitudes, i.e. the peak concentrations are now observed earlier in the year compared to previous decades with a rate of 3-6 days/decade. (Parrish et al., 2013). This shift is attributed to increasing emissions of O_3 precursors in developing countries, that led to an equatorward redistribution of precursors in the previous decades (Zhang et al., 2016). Negative trends of the 95th percentile of O_3 and positive trends for the 5th percentile have been detected across Europe (Yan et al., 2018). Simultaneous decrease of maximum concentrations in summer and increase in winter indicate a decrease of amplitude in the seasonal variation of O_3, probably as a result of the regulations in the 1990s (Simon et al., 2015).

O_3 variations are largely governed by climate and weather variability (Yan et al., 2018). Especially temperature influences O_3 concentrations in the troposphere, mainly by increasing the rates of several chemical reactions, and by increasing emissions of biogenic VOCs with increasing temperature (Sillman and Samson, 1995). Thermal decomposition of peroxyacyl nitrates (PANs) at high air temperature conditions results in elevated O_3 concentrations (Dawson et al., 2007). Indeed, extreme O_3 concentrations in central Europe are mainly associated with high temperatures (Otero et al., 2016). However, there are indications that the relationship of O_3 to temperature has changed in the last 20 years. For instance, in the U.S., O_3 climate penalty – defined as the slope of the O_3 versus temperature relationship – dropped from 3.2 ppbv/°C before 2002 to 2.2 ppbv/°C after 2002 as a result of NO_x emission reductions (Bloomer et al., 2009). Additionally, Colette et al. (2015), based on chemistry-transport and climate-chemistry model projections, assessed the impact of climate change on the climate penalty and found that over

European land surfaces summer O_3 change is [0.44; 0.64] and [0.99; 1.50] ppbv (95% confidence interval) for the 2041-2070 and 2071-2100 time periods, respectively.

At different locations, O_3 may show a different temporal evolution due to a variety of factors, such as local pollution, topography, influence of nearby sources or even trans-boundary transport of O_3 and its precursors. In addition, meteorological conditions can vary amongst different locations within large regions such as Europe, affecting O_3 concentrations in various ways. O_3 trend studies in the past have tried to tackle this issue, mainly by using clustering techniques to categorize European measurement sites based on different O_3 metrics (e.g. Henne et al. (2010)). For instance, a site type classification representing O_3 regimes between 2007 and 2010 was obtained by Lyapina et al. (2016) using mean seasonal and diurnal variations. In addition, a geographical categorization reflecting the synoptic meteorological influence on O_3 variation between 1998 and 2012 was obtained by Carro-Calvo et al. (2017). To tackle low spatial representation of urban and rural sites across large domains, i.e. mid-latitude North America, western Europe and East Asia, Chang et al. (2017) obtained a latitude dependent site classification with lower concentrations in western and northern Europe and higher concentrations in southern Europe. These studies indicate that the selected metric used to characterize O_3 in clustering leads to site classifications that represent different aspects of O_3 variability.

In the current study, a multidimensional clustering method that captures several influencing factors for the long-term trend of O_3 is presented. The temporal and spatial evolution of O_3 concentrations between 2000 and 2015 is studied using data provided by the European Environmental Agency (EEA). Mean O_3 concentrations are decomposed into the underlying frequencies based on a non-parametric time scale decomposition method to obtain the long-term (LT), seasonal (S) and short-term (W) variations. The multidimensional clustering approach is applied to the distinct frequency signals LT(t) and S(t) extracted from the observations.

In addition, long-term trends of de-seasonalized daily mean O_3 and meteo-adjusted peak O_3 concentrations are calculated. Through de-seasonalization and meteo-adjustment, a significant fraction of the meteorologically driven variability of O_3 is excluded from the observations, and uncertainty in the trend estimation is reduced by a large factor. Intersections of site groups, i.e. LT(t)-and S(t)-clusters, are employed to guide the study of O_3 long-term trends. Furthermore, changes in the amplitude and phase of the seasonal variability of O_3 are explored based on the S(t) signal obtained by the time scale decomposition methodology. Finally, long-term changes in the relationship between O_3 and temperature are estimated and discussed for the different site environments and regions in Europe.

2 Data

Data for O_3 surface measurements are provided by the EEA (Air Quality e-Reporting) in an hourly resolution for the period between 2000 and 2015. In this study, only time series with a maximum of 15% of missing values, and a maximum of 120 consecutive days with missing values are used for the whole period of measurements, leaving the study with 291 sites across the European domain (Fig. 1). The daily mean and the daily maximum of the 8 hour running mean based on hourly mean concentrations (MDA8 O_3) are calculated following the definition by the European Union Directive of 2008 (European Parliament and Council of the European Union, 2008). For the representation of peak concentrations the following metrics are used: (a) MTDM, which is the mean of the ten highest daily maximum O_3 concentrations ~~during~~ between May and September based on hourly mean data and (b) 4-MDA8, the mean of the four highest MDA8 O_3 concentrations per year.

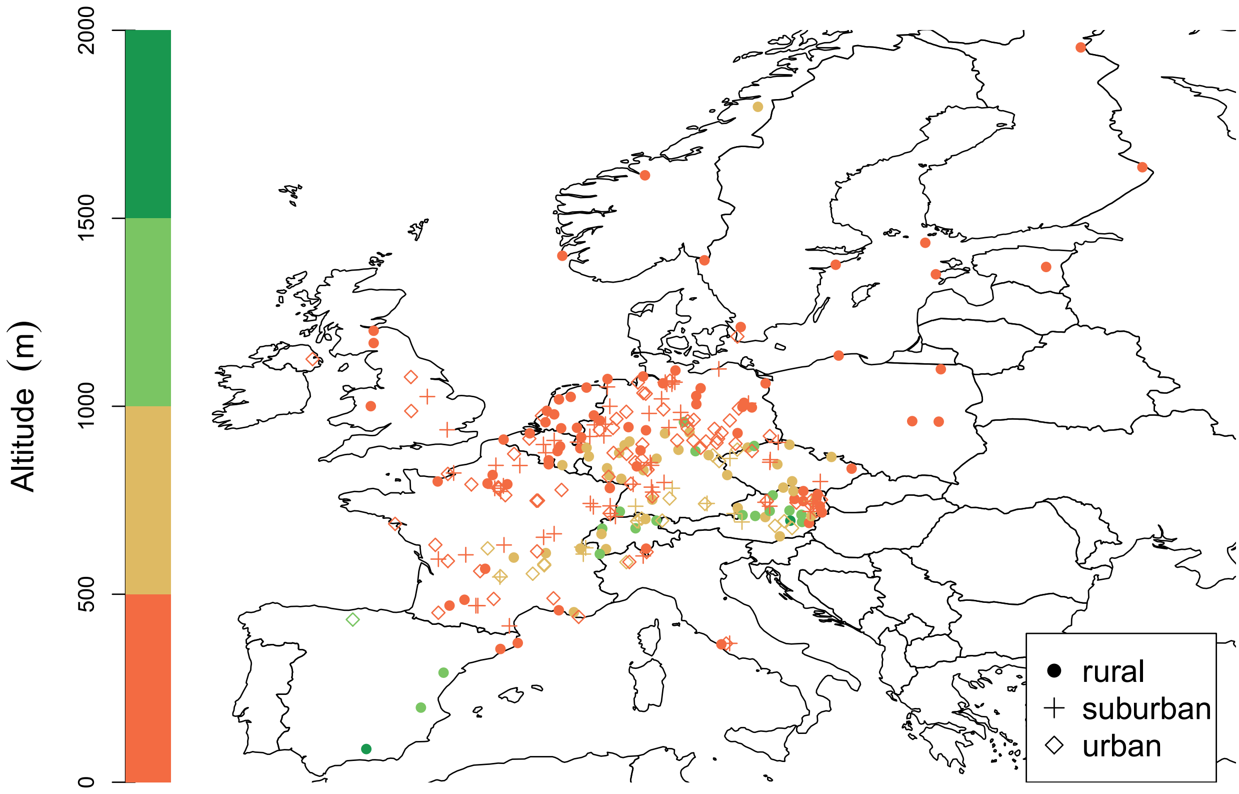

Figure 1. European map showing the location of the studied sites. Type of environment (symbols) and altitude (color bar) are indicated.

Meteorological variables are extracted from the ERA-Interim data-set on a 1 degree grid at the location (longitude-latitude-altitude) of each station and in 3-hourly intervals. The variables considered for the meteo-adjustment of the peak O_3 metrics are temperature (K), specific humidity (kg/kg^{-1}), surface pressure (hPa), boundary layer height (m), convective available potential energy (CAPE, $J \cdot kg^{-1}$), East-West surface stress ($N \cdot s \cdot m^2$) and North-South surface stress ($N \cdot s \cdot m^2$).

The present trend analysis focuses on (a) the de-seasonalized daily mean and MDA8 O_3 and (b) the meteo-adjusted MTDM and 4-MDA8 concentrations. The analysis of changes in the seasonal cycle of O_3 across Europe is based on the daily mean O_3 concentrations.

3 Methods

3.1 Time scale decomposition of daily mean and MDA8 O_3

Time scale decomposition refers to decomposition of the O_3 time series into the relevant underlying frequencies:

$$O_3(t) = LT(t) + S(t) + W(t) + E(t) \tag{1}$$

where $O_3(t)$ is the daily mean and MDA8 O_3 time series, $LT(t)$ the long-term variation, $S(t)$ the seasonal variation, $W(t)$ the short-term variation and $E(t)$ the remainder of the decomposition. Time scale decomposition in this study is performed with a non-parametric method, called the ensemble empirical mode decomposition (EEMD, Huang et al., 1998; Huang and Wu, 2008; Wu and Huang, 2009), which is considered a powerful method for decomposing O_3 time series (Boleti et al., 2018). The method detects the hidden frequencies in the time series based merely on the data and yields the so-called intrinsic mode functions (IMFs); each IMF represents one distinct frequency in the signal.

$$y(t) = \sum_{j=1}^{n} c_j(t) + LT(t) \tag{2}$$

where $y(t)$ is the input data, c_j the different IMFs, n the number of the IMFs and the remainder time series is the LT(t) of the input data. By adding together the IMFs with frequencies between around 40 days and 3 years we obtain the seasonal variation of O_3 (~~$S(t) = c_7 + ... + c_{10}$~~$S(t) = c_7(t) + ... + c_{10}(t)$) and by adding the frequencies that are smaller than 40 days the short-term variation is acquired (~~$W(t) = c_1 + ... + c_6$).~~ $W(t) = c_1(t) + ... + c_6(t)$). A more detailed discussion on the choice of the IMFs for the seasonal and short term variations can be found in the study by Boleti et al. (2018).

3.2 Cluster analysis of O_3 variations

Cluster analysis is referred to pattern recognition in high dimensional data. The main idea is to represent n objects by identifying k groups based on levels of similarity. Objects in the same group must have the highest level of similarity while objects from different groups must have low level of similarity (Jain, 2010). The partitioning around medoids (PAM) clustering algorithm is used in this study. It is based on k-means (MacQueen, 1967; Hartigan and Wong, 1979) which is a widely used clustering technique ~~(Lyapina et al., 2016, e.g.)~~(e.g. Lyapina et al. (2016)). PAM is more robust than k-means and less sensitive to outliers, because it ~~minimizes the sum of dissimilarities instead of the sum of squared euclidean distances~~ uses medoids (actual points in the data), instead of centroids (usually artificial points). (R Development Core Team, 2017). It works as follows: First, a set of n high dimensional objects (measurement sites) is clustered into a set of k clusters. Initially, k clusters are generated randomly and the empirical means m_k of the euclidean distance between their data points are calculated. Then, each data point is assigned to its nearest cluster center (centroid). Centroids are iteratively updated by taking the medoid of all data points assigned to their clusters. The squared error (ε) between the m_k and the points in the cluster (x_i) is calculated as:

$$\varepsilon = \sum_{i=1}^{n} \|x_i - m_k\|^2 \tag{3}$$

Each centroid defines one of the clusters and each data point is assigned to its nearest centroid, and the iterative process is terminated when the ϵ is minimized.

For identification of the clusters the LT(t), S(t) and W(t) of the daily mean and MDA8 O_3 were used as input time series in the PAM algorithm. A sufficient number of clusters must be defined in order to capture dominant behaviors such that redundant information is avoided but at the same time not overlooking important characteristics. To identify the optimal number of clusters the ~~k-means~~ PAM algorithm is iteratively executed for a range of k values (number of clusters) and the average sum of ϵ (SSE) is calculated for each iteration, i.e. each k.

$$SSE = \sum_{i=1}^{n} \varepsilon^2 \tag{4}$$

The number of clusters with the largest reduction in SSE is considered as the most representative. Eventually, the choice of the ideal number of clusters results from a combination of the SSE approach and interpretability of the obtained clusters. In addition, a Silhouette width (S_w) analysis is performed to assess the goodness of the clustering (Rousseeuw, 1987).

More details about the number of clusters, the goodness of the clustering and the S_w are provided in the supplementary material (Sections S1 and S2).

3.3 Daily mean and MDA8 O_3 long-term trend analysis

Meteorological adjustment is essential for calculation of robust O_3 long-term trends. Thus, daily mean and MDA8 O_3 observations are de-seasonalized by subtracting the S(t) obtained with the EEMD from the observations (Boleti et al., 2018)

$$y_d(t) = y(t) - S(t) \tag{5}$$

where $y_d(t)$ is the de-seasonalized time series and $y(t)$ the observations. Through de-seasonalization observations are adjusted for the effect of meteorology on the inter-annual time scale. Theil-Sen trends (Theil, 1950; Sen, 1968) are then calculated based on monthly mean de-seasonalized concentrations ~~of the~~ $y_d(t)$ for the period 2000-2015. The 95% confidence interval of the trend is obtained by bootstrapping. The Theil-Sen trends were estimated using the *openair* library in R (R Development Core Team, 2017).

3.4 Peak O_3 concentrations long-term trend analysis

Trend analysis of peak O_3 metrics is performed for the MTDM and the 4-MDA8 O_3, based on a meteo-adjustment approach as in Boleti et al. (2019). A different approach for meteorological adjustment was used for the peak O_3 than for the daily mean and MDA8~~, because~~ ; de-seasonalization is not meaningful for peak O_3 because peak ~~ozone~~ O_3 events are temporally localized. Thus, daily maximum and MDA8 O_3 observations were linked to the available meteorological variables through generalized additive models (GAMs, Hastie and Tibshirani, 1990; Wood, 2006). The models are fitted for the warm season ~~(~~May-September ~~)~~as by definition the MTDM refers to this period of the year. GAMs are instances of generalized linear models in which the model is specified as a sum of smooth functions of the covariates. A GAM can be described as:

$$O_3(t) = \alpha + \sum_{i=1}^{n} s_i\left(M_i\left(t\right)\right) + s_0(t) + \epsilon(t) \tag{6}$$

where $O_3(t)$ stands for the O_3 time series observations (daily maximum and MDA8), α is the intercept, s_i are the smooth functions (thin plates splines) of the numeric meteorological variables M_i and n denotes the number of the numeric meteorological variables in the GAM. The temporal trend is represented through the smooth function $s_0(t)$, where t is the time variable expressed by the Julian day. Finally, ϵ stands for the residuals of the model. For the GAMs, the following meteorological variables were used~~based on the meteorological variable selection performed by Boleti et al. (2019)~~: the daily maximum temperature, daily mean specific humidity, daily mean surface pressure, daily maximum boundary layer height, morning mean ~~convective available potential energy (CAPE)~~CAPE, daily mean East-West surface stress and daily mean North-South surface stress, as well as a time variable the Julian day. The above explanatory meteorological variables are the ones that were most often selected in the Swiss sites by the meteorological variable selection performed by Boleti et al. (2019). The GAMs were estimated with the *mgcv* library in R (R Development Core Team, 2017).

The meteo-adjusted daily maximum and MDA8 O_3 concentrations were calculated similar to Barmpadimos et al. (2011) as:

$$O_{3_{metadj}}(t) = \alpha + s_0(t) + \epsilon(t) \tag{7}$$

where α is the intercept of the model, $s_0(t)$ the time variable as Julian day, and $\epsilon(t)$ the residuals. The meteo-adjusted MTDM and 4-MDA8 concentrations were estimated based on the meteo-adjusted values ($O_{3_{adj}}(t)$) on the same days as they were identified before the meteo-adjustment. Eventually, meteo-adjusted trends were calculated with the Theil-Sen trend estimator applied on the $O_{3_{metadj}}(t)$.

3.5 O_3 seasonal cycle trend analysis

The S(t) signal extracted with the EEMD captures the meteorologically driven O_3 variation on yearly to multi-year time scales, and is more representative compared to parametric fitting approaches (Boleti et al., 2018). Here, changes in the daily mean S(t) of O_3 throughout the studied period are identified as follows: the maximum and minimum O_3 value as well as the day when the maximum O_3 occurred in each year are identified in the S(t), referred here as S_{max}, S_{min} and S_{DoM} respectively (Fig. 2). A Theil-Sen trend estimator for each of the $S_{max}(t)$, $S_{min}(t)$ and $S_{DoM}(t)$ is applied for each site cluster, representing the long-term temporal evolution of the amplitude and phase of S(t).

3.6 Relationship between O_3 and temperature

The relationship between O_3 and temperature is studied for the warm season May-September. A linear regression model between daily maximum O_3 concentrations and daily maximum temperature is applied for each year throughout the studied period 2000-2015 as:

$$O_3(t)_i = \beta_{0i} + \beta_{1i} \cdot T(t)_i, i = 1, 2, ..n \tag{8}$$

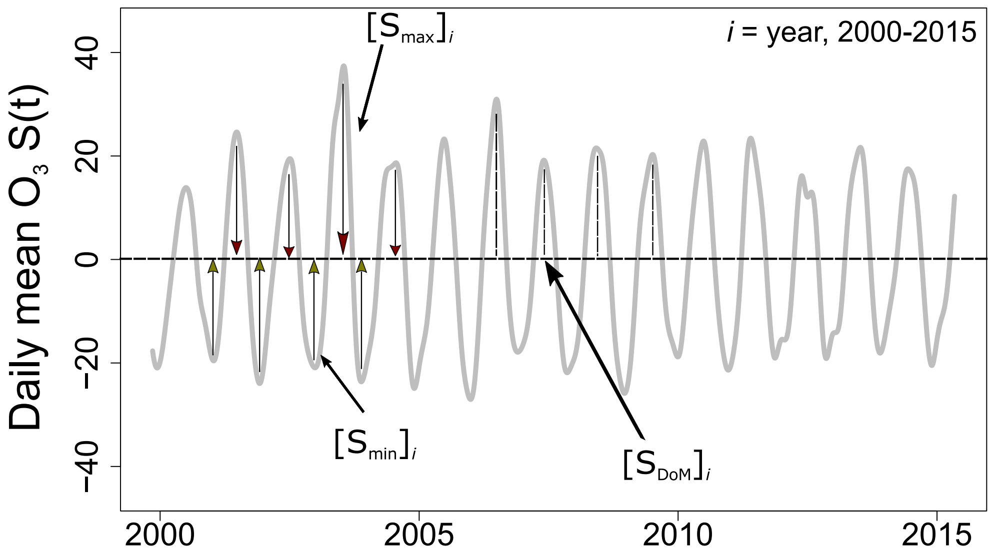

Figure 2. Schematic illustration for explaining the estimation of the ($S_{max}(t)$ and $S_{min}(t)$) and the annual day of maximum of the seasonal signal ($S_{DoM}(t)$) as calculated from the daily mean O_3 time series.

where $O_3(t)$ is the time series of the daily maximum O_3, $T(t)$ the time series of the daily maximum temperature and n is the number of years. β_{0i} is the intercept and $\beta_{1i}(t)$ the parameter describing the linear effect of temperature on O_3. Then, a linear model is applied to $\beta_{1i}(t)$ over all years for each site cluster to identify the long-term trend of the slope between O_3 and temperature maximum values. In addition, a linear regression model is applied on the daily maximum O_3 concentrations against binned temperature ranges and in three consequent time periods (2000-2005, 2005-2010 and 2010-2015).

4 Results

4.1 Cluster analysis

Here, we present the results of the daily mean LT(t)- and S(t)-clustering; results for the W(t)-clustering and the cluster analysis based on the MDA8 are provided in the supplementary material (Section S3). The clusters based on daily mean and MDA8 O_3 are rather similar, thus, the choice of clusters based on these two metrics does not affect the conclusions. The daily mean O_3 clusters depict the main influencing factors for O_3 trends, i.e. proximity to emission sources and meteorological conditions. Therefore, it is appropriate to study long-term trends based on the O_3 daily mean clusters. Application of the clustering algorithm to the LT(t) leads to a site type classification, which largely reflects the proximity to emission sources of O_3 precursors.

S(t)- and W(t)-clustering leads to a regional site classification, which reflects the importance of the climate on the annual cycle of O_3. It is observed that a few sites have a negative S_w, which means that these sites are assigned to a certain cluster although they do not really fit into any of the identified clusters (see supplementary material sections S2 an S5). Nevertheless, the sites with negative S_w were not excluded from the data analysis as they do not have a noticeable influence on the results.

O_3 concentrations often increase with distance from emission sources of NO_x. Thus, LT(t)-clustering leads to identification of site groups with similar type of environment in terms of proximity to precursor emissions and mean O_3 concentrations, which are indicative of multiannual changes in the O_3 time series (Boleti et al., 2018). This measurement-based classification can be more informative than reported station types, since e.g. there are rural sites with nearby pollution sources or even sites with surroundings that might have changed dramatically with time. In the following section, clusters obtained from analysis of daily mean O_3 are presented and discussed in detail; the clusters derived from MDA8 O_3 are similar and presented in the supplementary material (Section S3).

Cluster analysis of the long-term variation LT(t) resulted in four clusters that mainly differ in the daily mean O_3 concentration levels: Cluster 1 includes sites that are marked in the Air Quality e-Reporting data repository as being of rural site type and sites that are mostly located at ~~higher~~ relatively high altitudes (on average 800 to 1200 m). The sites in cluster 1 show the highest O_3 concentrations as illustrated in Fig. 3. The high mean O_3 concentrations indicate that the sites in cluster 1 are representing background situations with minor influence of nearby emissions of man-made O_3 precursors. This cluster is therefore denoted as background cluster ("BAC"). Cluster 2 includes mostly rural sites, that are located at lower altitudes of around 300-600 m and is therefore labelled as rural cluster ("RUR") 3. The sites in cluster 3 are also located at low altitudes (around 100 to 300 m) and represent rural, suburban and urban site types in similar numbers. The sites in cluster 3 seem to be influenced by nearby man-made emissions of O_3 precursors such as NO_x, leading to lower mean O_3 concentrations compared to the sites in the "RUR" cluster. Cluster 3 consists of moderately polluted sites and denoted as cluster MOD. Finally, cluster 4 consists mostly of urban and suburban sites showing the lowest daily mean O_3 concentrations likely due to the proximity to sources of NO_x emissions and the resulting enhanced depletion of O_3 through reaction with NO. Consequently, cluster 4 is denoted as the highly polluted cluster ("HIG").

The LT(t) signal as derived from the daily mean (Fig. 3) and MDA8 O_3 (Fig. S9) observations increases for "BAC" and "RUR" until around beginning of 2000s and decreases afterwards. For the "MOD" and "HIG" clusters the same pattern was observed, but the decrease starts much later than in the rural sites, i.e. around end of 2000s. Especially in the "HIG" sites mostly a level-off is observed after 2010 rather than a decrease. Similar temporal evolution with inflection points in the LT(t) has been observed in the study by Boleti et al. (2018) which was focused on trends of average O_3 concentrations in Switzerland.

Clusters derived from the daily mean S(t) show a regional representation most likely due to the influence of the ~~climatic~~ regional climate conditions an the annual cycle of O_3. The following five clusters were obtained from the daily mean S(t) (Fig. 4): (1) "CentralNorth" comprises northern and eastern part of Germany, Netherlands and some eastern sites in Czech Republic, Poland and Austria, (2) "CentralSouth" covers most part of Austria, Switzerland and some sites in the Southwest of Germany, (3) "West" incorporates the biggest part of France, Belgium and Spain, (4) "PoValley" includes the sites located in the Po Valley, an industrial region in Northern Italy. (5) "North" covers most of the UK and Scandinavia. The number of sites included in each

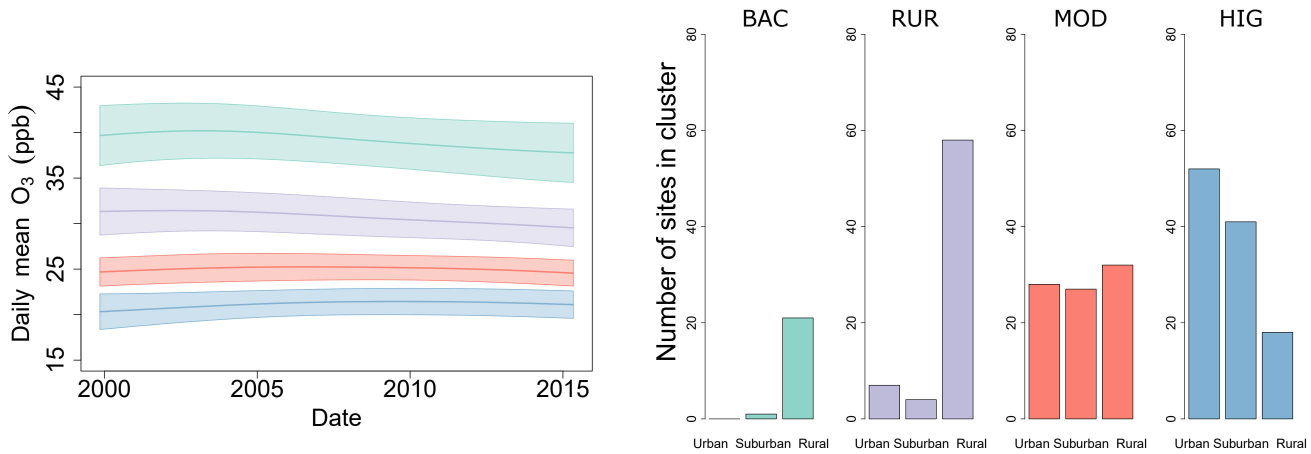

Figure 3. Clusters based on daily mean O_3 LT(t). Average LT(t) in each cluster with $\pm$ the standard deviation (left) and histograms for the site type included in each cluster.

cluster are shown in Table 1. The sites in "PoValley" display the most pronounced S(t), mainly due to the Mediterranean weather conditions, e.g. high temperatures. At the same time high NO_x and VOC emissions in this region leads to higher O_3 concentrations. Special topographic conditions (valley south of Alps) in combination with cyclonic systems lead to containment of emissions from the Milan industrial area in Po Valley (Bärtsch-Ritter et al., 2004; Henne et al., 2005; Prévôt et al., 1997; Thunis et al., 2009 . The "North" cluster has the smallest seasonal variability, due to generally low O_3 concentrations, and lower temperature conditions in this region. Especially in the Scandinavian sites meteorological conditions are rather unfavorable for O_3 formation. Also, the regions included in the "North" cluster are influenced by cyclonic systems arriving in Europe through the North Atlantic ocean, that carry air pollutants into Europe (Stohl, 2002; Dentener et al., 2010). Thus, the influence of background O_3, i.e. O_3 inflow from northern America and eastern Asia, is high in these sites (Derwent et al., 2004, 2013). In all clusters (except in the "North") the hot summers of 2003 and 2006 are visible in the S(t) signal, which shows that the S(t) signal can capture important events in O_3 variability that are driven by seasonal meteorological phenomena. It is interesting to note that both Central North sites have seasonal values in their signal comparable to the Po Valley values, probably related to industrial and agricultural emissions in the area of Northern Germany.

Annual cycle of daily mean O_3 S(t) for the daily mean S(t) clusters.

A two-dimensional classification scheme is achieved by employing the LT(t)- and S(t)-clusters. Our results are in good agreement with previous classification studies, where by using different O_3 metrics similar classifications have been obtained. For instance, the spatial analysis based on gridded O_3 data (MDA8) across Europe by Carro-Calvo et al. (2017) resulted in a regional site classification. The gridded data used by Carro-Calvo et al. (2017) were obtained by spatial interpolation leading to a larger and regular geographical coverage compared to the available observations. Compared to Carro-Calvo et al. (2017), similar geographical clusters were identified here, except for the Iberian Peninsula, eastern Europe, northern Scandinavia and the Balkan states that do not appear as separate clusters in our analysis. This is most probably due to the small number of observational

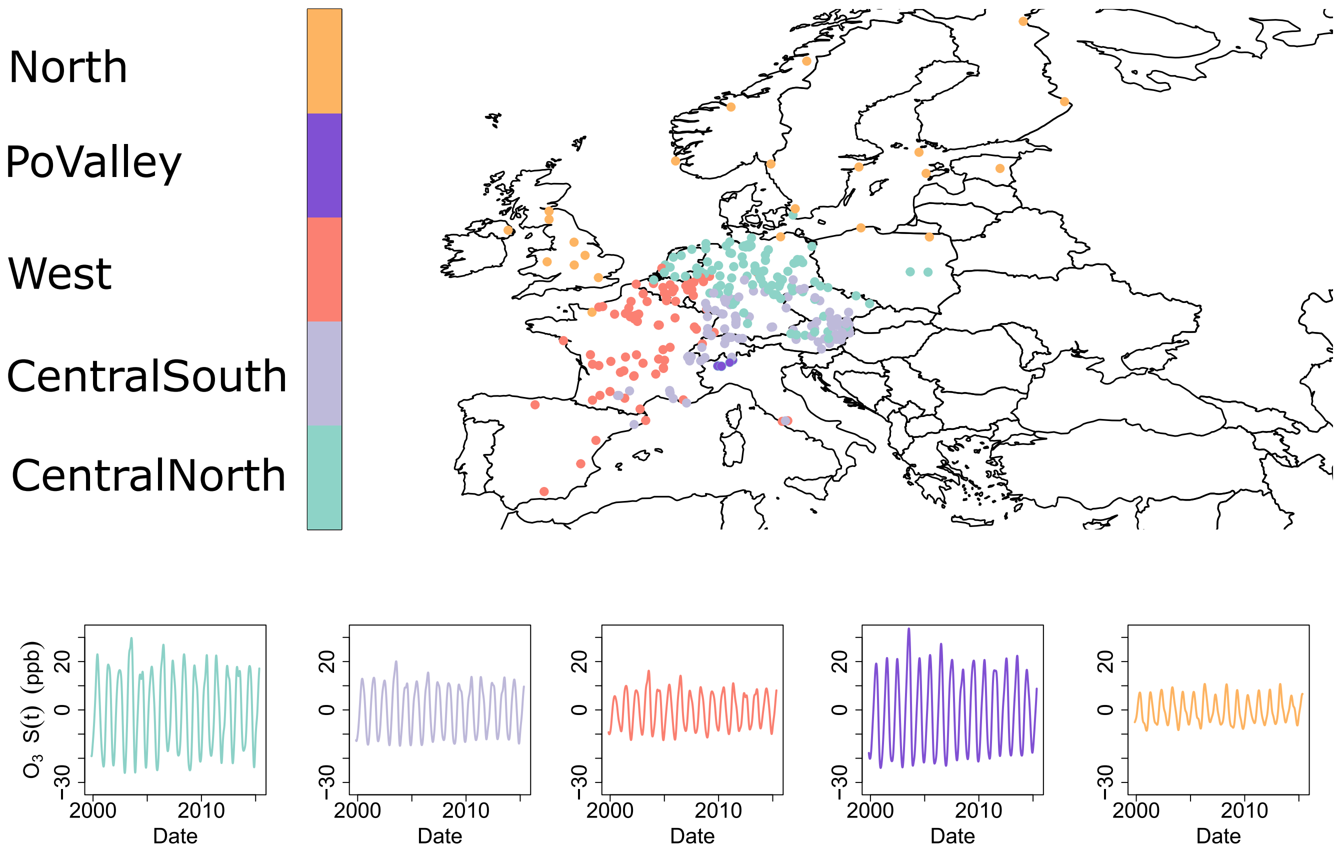

Figure 4. Map with the site clusters derived from daily O_3 S(t), and average S(t) in each site cluster.

sites in the above regions. More specifically, the sites in the "West" cluster correspond to the Western European and the Iberian Peninsula clusters as extracted by Carro-Calvo et al. (2017), the "North" cluster covers the British Isles, northern Scandinavia, the Baltic region and parts of the north-central Europe clusters of Carro-Calvo et al. (2017). Moreover, the "CentralNorth" cluster includes the north-central, and eastern Europe and parts of the south-central clusters, while the "CentralSouth" cluster corresponds to the south-central cluster of Carro-Calvo et al. (2017). Finally, the "PoValley" cluster is embedded in the south central cluster of Carro-Calvo et al. (2017). In contrast to our study, gridded MDA8 O_3 concentration during summer have exclusively been used for the cluster analysis by Carro-Calvo et al. (2017), therefore conditions when the correlation of O_3 and meteorological variables such as temperature is typically strongest. In addition, the present study results in spatial classification by utilizing the seasonal variation, while Carro-Calvo et al. (2017) have used normalized anomalies. Four site type clusters were found based on the LT(t) in this study , which are similar to the similar to Lyapina et al. (2016) based on absolute mixing ratios of O_3 variations, which identified five site type clusters identified by Lyapina et al. (2016)ranging from urban traffic (as the "HIG" cluster here) to rural background environments (equivalent to "RUR"). Similar site classifications are obtained because the L(t) signal of this study and the mean seasonal and diurnal profiles of Lyapina et al. (2016) both capture the O_3 concentration levels distinguishing specific pollution regimes.

Table 1. Number of sites in each site group based on the LT(t) and S(t) clusters.

Cluster	**BAC**	**RUR**	**MOD**	**HIG**	**Sum**
CentralNorth	5	8	33	48	94
CentralSouth	8	29	27	28	92
West	9	16	21	31	77
PoValley	0	2	2	0	4
North	0	16	4	4	24
Sum	22	71	87	111	Total: 291

4.2 Trends of daily mean O_3 concentrations

The daily mean LT(t)- and S(t)-clusters identified in section 4.1 are used for assessment of the temporal trends for the different site types and geographical locations. Overall, decreasing daily O_3 trends means are found for rural sites, while there is a tendency for increasing O_3 in more polluted urban environments (Fig. 5). The number of sites that belong in each of the identified groups is shown in Table 1. MDA8 trends are similar to the daily mean trends, thus, are shown in the supplementary material Section S4). In 64% of all sites significant trends (p-value<0.05) were identified for the daily mean O_3; 61% among the significant trends were negative and 39% positive.

Most rural sites – "BAC" and "RUR" – experienced decreasing daily mean O_3 concentrations in all regions, as expected following the NO_x and VOC reductions in Europe (Fig. 5). At the "MOD" and "HIG" sites a levelling-off or increase is observed respectively, especially in "CentralNorth", "West" and "North" regions. At the "HIG" sites the positive trends can be partly could partly be explained by the increase of NO_2 to NO_x ratio, originating from the proliferation of diesel vehicles, that have increased in the European car fleet (EEA, 2009). In addition, the strong reduction of NO_x concentrations that led to less titration of O_3 by NO, could also explain the positive trends at urban and suburban sites. The late inflection point at urban sites (LT(t) of "HIG" cluster in Fig. 3) can be an additional effect of the reduced titration of O_3, which leads to positive trends at the "HIG" sites. Flat trends at central European sites, might partially be explained by the increasing influence of North American and Asian emissions, that have counterbalanced the decrease of European NO_x and VOC concentrations (Derwent et al., 2018; Yan et al., 2018).

In agreement with our results, significant decreases of daytime average and summertime mean of MDA8 O_3 at European rural sites and as well as small and non-significant downward trends of MDA8 at urban sites have been found previously for the time period 2000-2014 (Chang et al., 2017). Similarly, in a report by EEA (2016) it was found that between 2000 and 2014 annual mean O_3 and annual mean MDA8 O_3 have been decreasing in rural background sites, while at more polluted sites influenced by nearby man-made precursor emissions, upward trends have been detected.

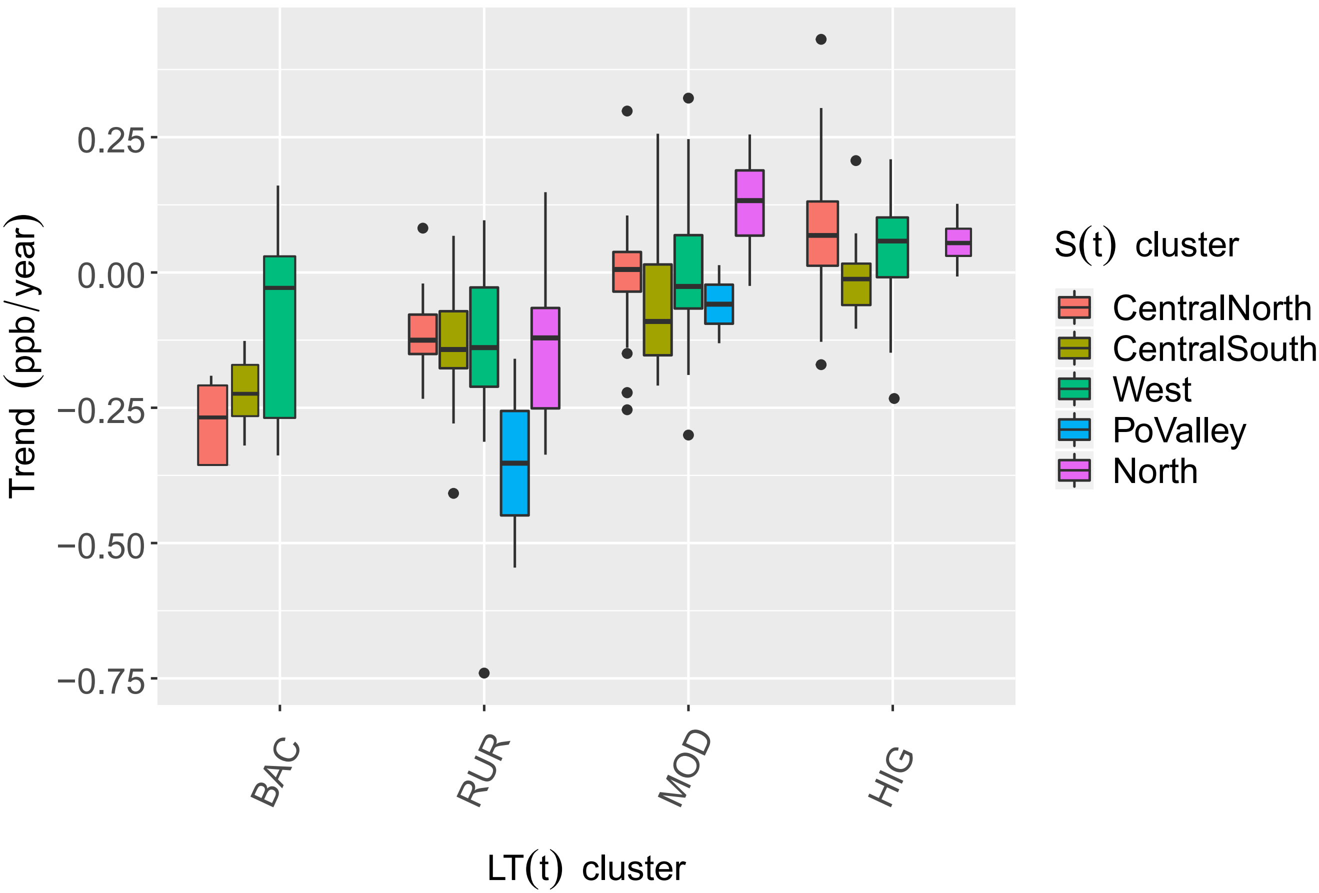

Figure 5. Box-plots of de-seasonalized daily mean O_3 trends for the LT(t)- and S(t)-clusters. LT(t)-clusters represent a site type classification while the S(t)-clusters a geographical one that is influenced by climatic regional climate conditions. Boxes include 25th to 75th percentiles with the line indicating the median value; whiskers extend to 1.5 times the interquartile range.

Number of sites in each site group based on the LT(t) and S(t) clustersClusterBACRURMODHIG SumCentralNorth 5 8 33 48 94 CentralSouth 8 29 27 28 92 West 9 16 21 31 77 PoValley 0 2 2 0 4 North 0 16 4 4 24 Sum 22 71 87 111 Total: 291

O_3 trends at sites in the cluster "North" indicate changes in background O_3, especially in the "RUR" ones that are mostly free from local emissions. Here, decreasing trends of daily mean O_3 were found in "RUR" sites, while in the "MOD" and "HIG" the trends are slightly increasing. It is interesting to compare the trends in the "North" cluster with the temporal evolution of O_3 in Mace Head (remote station in northwestern Ireland), which is representative for inflow of background O_3 into Europe. For this reason, we estimated the LT(t) variation of MDA8 O_3 and the Theil-Sen trend for the site in Mace Head (Fig. 6) . An to compare with the MDA8 O_3 trend identified by Derwent et al. (2018). Here, an inflection point was identified in the LT(t) in 2006, i.e. MDA8 O_3 has been increasing between 1988 and 2006 and started to slightly decline after 2006. De-seasonalized Theil-Sen trends were estimated 0.08 ppb/year [0.06,0.1] for the first period and -0.04 ppb/year [-0.09,0.02] for the second period.

Similarly, Derwent et al. (2018) have found an increase of 0.34 ± 0.07 ppb/year with a deceleration rate after 2007 of -0.0225 $\pm$ 0.008 ppb/year^2 at the same station, based on a combination of filtered measurement data and modeling output (Lagrangian dispersion). The inflection point in mid-2000s might be the reason for the flat trend of the annual average O_3 during 2000s as estimated by Derwent et al. (2013).

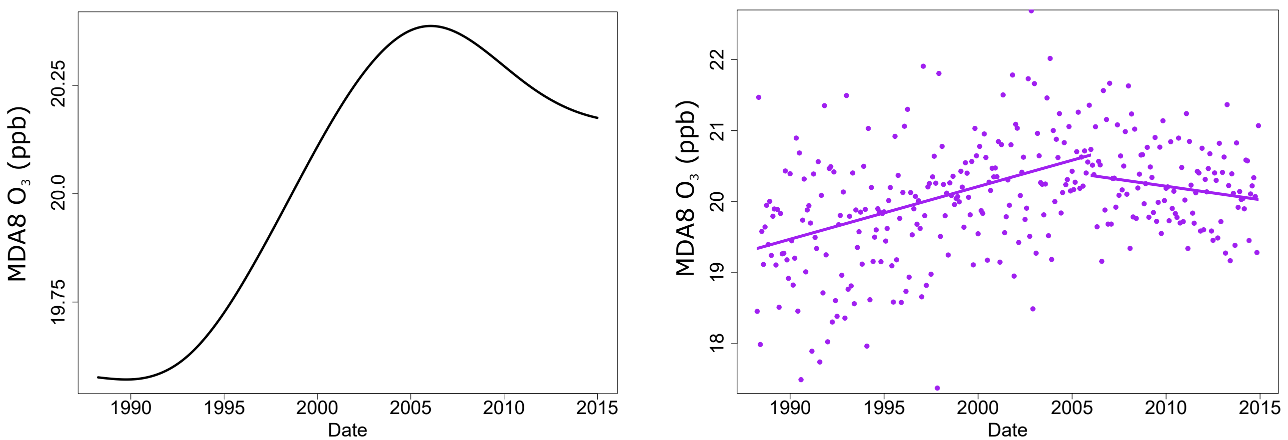

Figure 6. MDA8 LT(t) in Mace Head extracted with the EEMD (left) and the corresponding de-seasonalized Theil-Sen trend (right).

4.3 Trends of peak O_3 concentrations

Peak O_3 concentrations in summertime are attributed to ~~increased~~ photochemical production during this time of the year, and the spring maximum in remote locations is linked to ~~increased~~ stratospheric influx as well as hemisphere-wide photochemical production during that season (Holton et al., 1995; Monks, 2000). In this study, significant negative meteo-adjusted MTDM trends were observed at 62% of the sites (ratio of sites with negative trends/number of all sites), while without meteo-adjustment significant negative trends were identified at only 19% of the sites (4-MDA8 trends are shown in the supplementary material Section S4). The higher number of sites with significant trends after the meteo-adjustment indicates the advantage of using meteo-adjusted observations in the trend estimation. This argument is supported in the study by Fleming et al. (2018), where significant negative trends of the 4th highest MDA8 O_3 between 2000 and 2014 have been detected at only 18% of the studied sites across Europe, while at a large proportion of sites either weak negative to weak positive or no trends at all were found. The non-significant trends have been attributed by Fleming et al. (2018) to the influence of meteorology which is not considered in their trend estimation.

Trends of meteo-adjusted MTDM are discussed here for the daily mean O_3 LT(t)- and S(t)-clusters. MTDM decreased for all site types and regions during the studied period 2000-2015. However, in the "RUR" cluster MTDM showed the strongest decrease among all LT(t)-clusters (Fig. 7). Interestingly, in the "BAC" cluster (especially the "West" cluster) the decrease of MTDM was not so pronounced, likely due to the increase of hemispheric transport of O_3 in Europe (Derwent et al., 2007; Vingarzan, 2004). The same pattern was observed at the high alpine site of Jungfraujoch, which is representative for European continental background O_3 concentrations (Balzani-Lööv et al., 2008; Boleti et al., 2019). Also, "HIG" sites in "CentralSouth" showed slightly smaller decrease of MTDM compared to the other regions, possibly due to industrialization in the neighboring eastern Europe (Vestreng et al., 2009). Nevertheless, in order to estimate the reasons and quantify the exact influence of the above factors on the trends, dedicated modelling studies are needed.

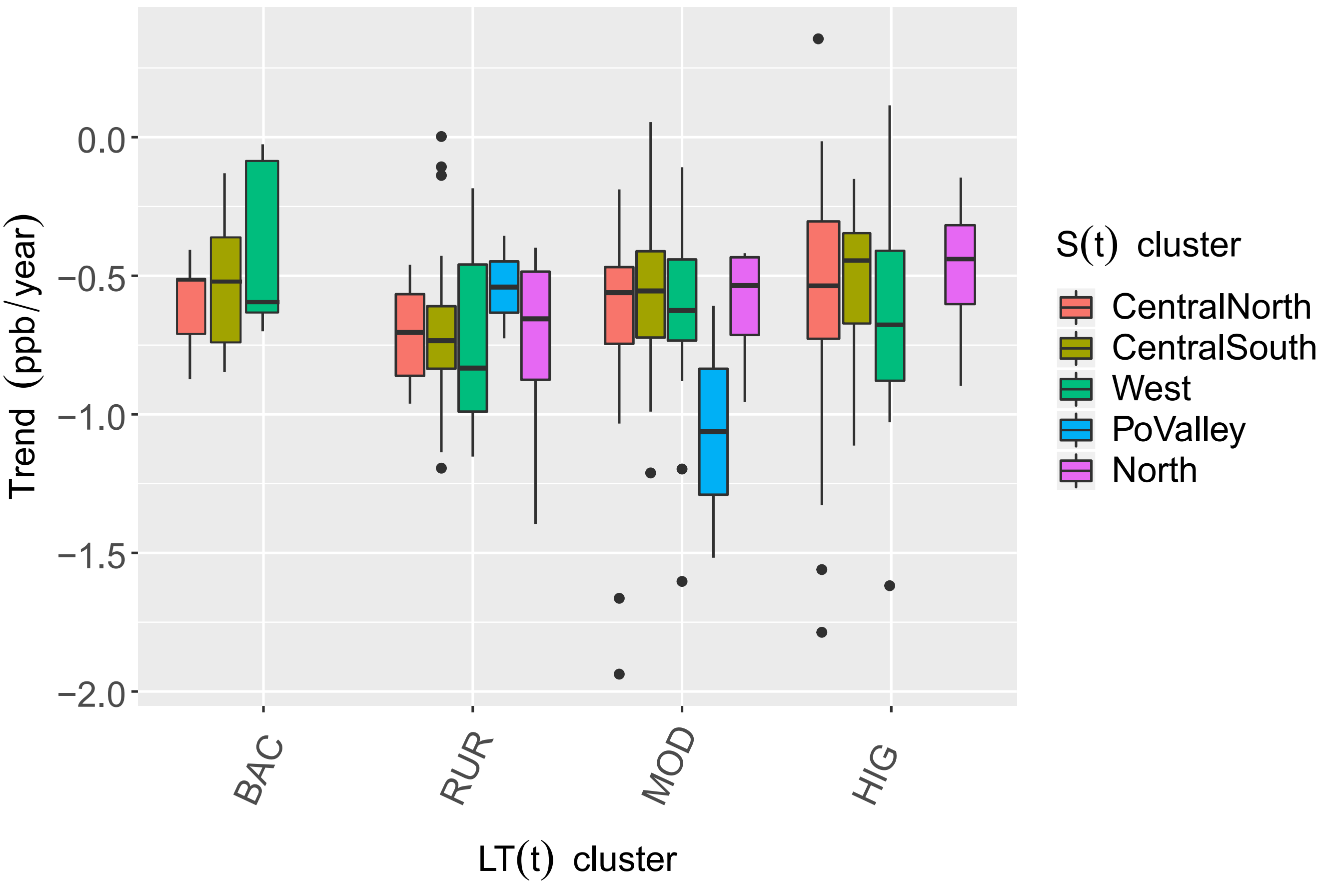

Figure 7. Box-plots of meteo-adjusted MTDM trends for the daily mean O_3 LT(t)- and S(t)-clusters. LT(t)-clusters represent a site type classification while the S(t)-clusters a geographical one that is influenced by ~~climatic~~ regional climate conditions.

Our results are in line with a modeling sensitivity study, where negative trends of the 95th percentile of O_3 concentrations were found in European rural background sites for the period 1995-2014 (Yan et al., 2018). For the shorter time period between 1995 and 2005, downward trends of measured MTDM have been observed for most parts of Europe as well (in the range [-0.12,-0.55] ppb/year), with the highest decrease in the Czech Republic, UK and the Netherlands (on average -1 ppb/year) and very small (nearly flat) in Switzerland (EEA, 2009). In our study, measured MTDM trends (2000-2015) for these regions are in the same range, i.e. the average decrease was estimated between -0.28 and -0.55 ppb/year. Smaller trends in Switzerland and central Northeast and northeast Germany have been observed by EEA (2009), which agrees with our result for the "CentralSouth" sites that showed the smallest average trend among all clusters. The flat trend in Switzerland during 1995-2005 is probably linked to the disproportional decrease of NO_x and VOCs until beginning of 2000s, when an inflection point has been observed at most polluted sites (Boleti et al., 2018). In Germany, a mixed behavior was observed by EEA (2009), with the northeastern part showing a stronger decrease and the central Northeast and northeast region a smaller decrease. Similar to our differentiation between the clusters, average MTDM trends within the "CentralNorth" cluster (with northern and northeastern Germany included) were higher and within the "CentralSouth" (covering central parts of Germany) lower.

4.4 O_3 seasonal cycle trends

Analysis of S(t) allows studying the characteristics of the annual cycle of O_3 without influence of short-term meteorological phenomena and long-term variations. Here, the trends of $S_{max}(t)$, $S_{min}(t)$ and $S_{DoM}(t)$ are presented for the five regions identified based on S(t) as calculated from daily mean O_3. In Fig. 8 the average annual O_3 cycles are shown; it is clear that in Po Valley the day of maximum O_3 occurs in summer (June-July), while in the North occurs around spring time (late March-April). This agrees with previous studies that have reported that both the highest average O_3 concentrations and extreme O_3 episodes tend to occur over the central and southern parts of Europe during summer while over northern Europe during spring (Schnell et al., 2015; Ordóñez et al., 2017). A declining amplitude of S(t) and simultaneously a phase shift towards an earlier time in the year can be observed for the 2000 to 2015 period (Table 2).

More specifically, an overall decrease in O_3 $S_{max}(t)$ by around 0.05-0.18 ppb/year and a simultaneous increase of $S_{min}(t)$ with a rate of around 0.25 ppb/year was observed for all S(t)-clusters (Fig. 9). However, in the "North" cluster the decrease of the $S_{max}(t)$ was very small and non-significant, probably due to the pronounced influence of background O_3 at these sites. The most pronounced shortening of S(t) amplitude can be seen at the "PoValley" sites, where the downward trend of peak O_3 is largest (Fig. 7). The increase in the $S_{min}(t)$ may be partially due to the decreased titration of O_3 after reductions of NO_x emissions and probably due to the increased influx of O_3 towards north and northwest Europe and more cyclonic activity in the north Atlantic during winter as well (Pausata et al., 2012). A decrease of the 95th percentile and an increase of 5th percentile of O_3 for the period 1995-2014 has been also identified in the EMEP network (rural background sites) (Yan et al., 2018). Lower summertime peaks as a result of decreased photochemical production and higher O_3 concentrations during the winter months due to decreased O_3 titration have been found in European air masses between 1987 and 2012 (Derwent et al., 2013) as well.

The trend of O_3 $S_{DoM}(t)$ is for all regions negative, i.e. the occurrence of the day of maximum O_3 has shifted to earlier days within the year with a rate of -0.47 to -1.35 days/year (Table 2, Fig. 10). The observed shift of the day of seasonal maxi-

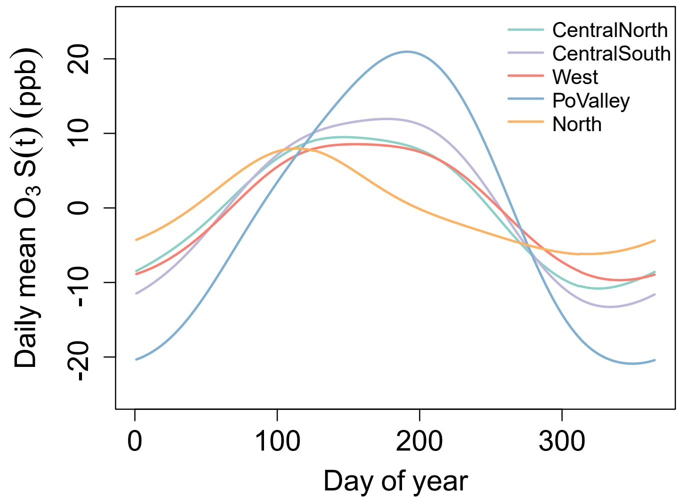

Figure 8. Annual cycle of daily mean O_3 S(t) for the daily mean S(t) clusters.

mum might be linked to the increase of emissions in East Asiathat have . The associated strong photochemical reaction rates, convection and NO_x sensitivity in the tropics and subtropics (Derwent et al., 2008; West et al., 2009; Fry et al., 2012; Gupta and Cicerone, have probably contributed to increased transport of air pollution to middle-and middle and northern latitudes (Zhang et al., 2016)where the effect on O_3 is probably greater due to greater convection, reaction rates and NO_x sensitivity (Derwent et al., 2008; West et . In addition, changes in meteorological factors may have affected the seasonal variation of O_3. For instance, a similar behavior with an earlier onset of the summer date (the calendar day on which the daily circulation/temperature relationship switches sign) has been observed by Cassou and Cattiaux (2016) using observational data, while Peña-Ortiz et al. (2015) have found that summer period is extending with a rate of around 2.4 days/decade based on gridded temperature data in Europe. The positive phase of the NAO leads to increased O_3 concentrations in Europe through higher westerly winds enhanced transport of O_3 and precursors across the North Atlantic , and enhanced transport of air pollutants from North America to Europe (Creilson et al., 2003). Changes in the NAO have led to increased westerly flow over the North Atlantic during the 1980s and 1990s, which in turn resulted to elevated OCreilson et al. (2003). An increase in baseline O_3 in northwestern Europe especially in winter and spring time (Pausata et al., 2012). related to the prevailing positive NAO Index -and the associated westerly flow and intercontinental transport- during 1990s and beginning of 2000s is probably a factor contributing to the increase of the winter S_{min} O3 values (Pausata et al., 2012). The enhanced hemispheric transport of air pollutants from North America to Europe is related to more increased transport through frontal systems as well (Creilson et al., 2003; Eckhardt et al., 2003). Increased O_3 in winter and spring, but not in summer, might lead to a shifting from a pronounced maximum in late summer to a broader spring-summer peak (Cooper et al., 2014). At the "West' sites a slightly stronger shift of the S_{DoMax} was observed

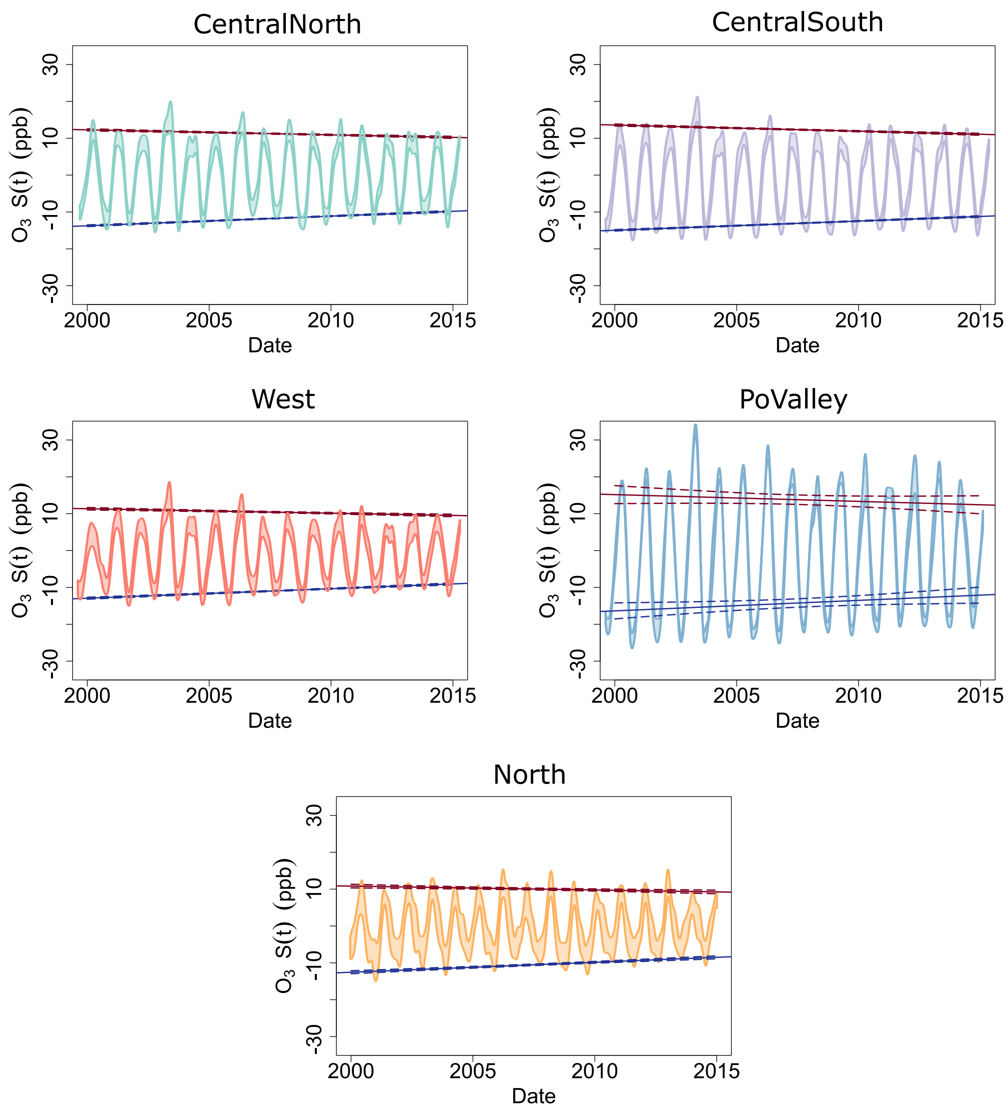

Figure 9. Temporal evolution of S_{max} and S_{min} for the daily mean O_3 S(t) clusters together with the average S(t) (bands indicate the average ~~*pm*~~ $\pm$ the standard deviation). Lines show the linear trends of S_{max} and S_{min} and dashed lines the 90% confidence interval.

compared to other clusters, while at the "North" sites the decrease was the smallest. The early spring maximum in the "North" sites in April (Fig. 8) can be explained by ~~higher~~ elevated NO_x that is released from PAN and alkyl nitrates that are produced during winter at northern latitudes (Brice et al., 1984; Bloomer et al., 2010).

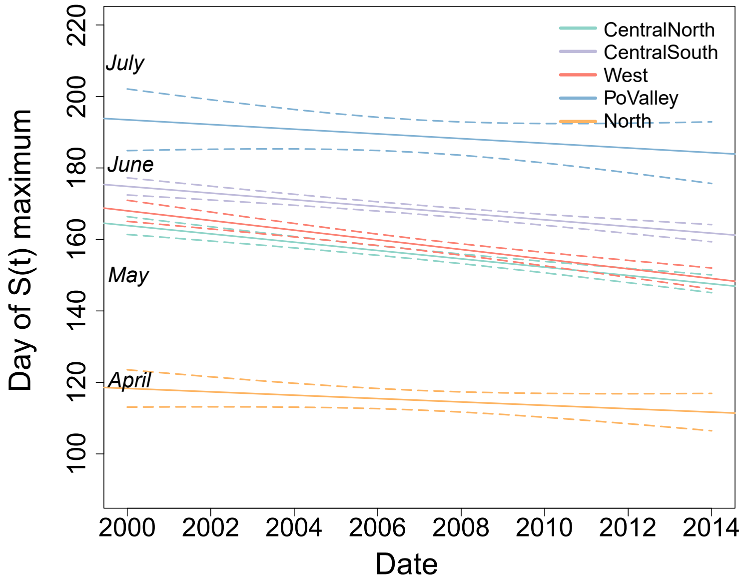

Figure 10. Linear trends of the S_{DoMax} for the daily mean S(t) clusters (dashed lines show the 90% confidence interval).

Table 2. Linear trends of S_{max}, S_{min} and ~~S_{DoMax}~~ S_{DoM} for the daily mean O_3 S(t) clusters during 2000-2015. $**$ indicate highly significant trend (p-value< 0.01), $*$ significant (p-value< 0.05) and $-$ indicate non-significant trend (p-value> 0.05).

Daily mean O_3 S(t)-Cluster	**Trend S_{max} (ppb/year)**	**Trend S_{min} (ppb/year)**	**Trend ~~S_{DoMax}~~ S_{DoM} (days/year)**
CentralNorth	-0.14 $\pm$ 0.04 (**)	0.26 $\pm$ 0.03 (**)	-1.16 $\pm$ 0.18 (**)
CentralSouth	-0.17 $\pm$ 0.03 (**)	0.25 $\pm$ 0.02 (**)	-0.93 $\pm$ 0.17 (**)
West	-0.12 $\pm$ 0.04 (**)	0.26 $\pm$ 0.03 (**)	-1.35 $\pm$ 0.21 (**)
PoValley	-0.18 $\pm$ 0.6 (-)	0.30 $\pm$ 0.56 (-)	-0.65 $\pm$ 0.61 (-)
North	-0.05 $\pm$ 0.1 (-)	0.24 $\pm$ 0.07 (**)	-0.47 $\pm$ 0.38 (-)

4.5 O_3 and temperature relationship

The O_3 sensitivity to temperature is a useful metric for validation of precursor reduction scenarios and emission inventories in chemistry-transport models (Oikonomakis et al., 2018). Here, we present the long-term trends of the relationship between the daily maximum O_3 concentrations and daily maximum temperature during the warm season from May to September between 2000 and 2015. Daily maximum O_3 and temperature are chosen in order to represent peak O_3 concentrations formed during the considered days.

Decreasing sensitivity of O_3 with respect to temperature was observed during the considered time period in all regions (Fig. 11). Fig. 11 shows the decreasing slopes of linear regression lines of maximum O_3 against temperature for successive

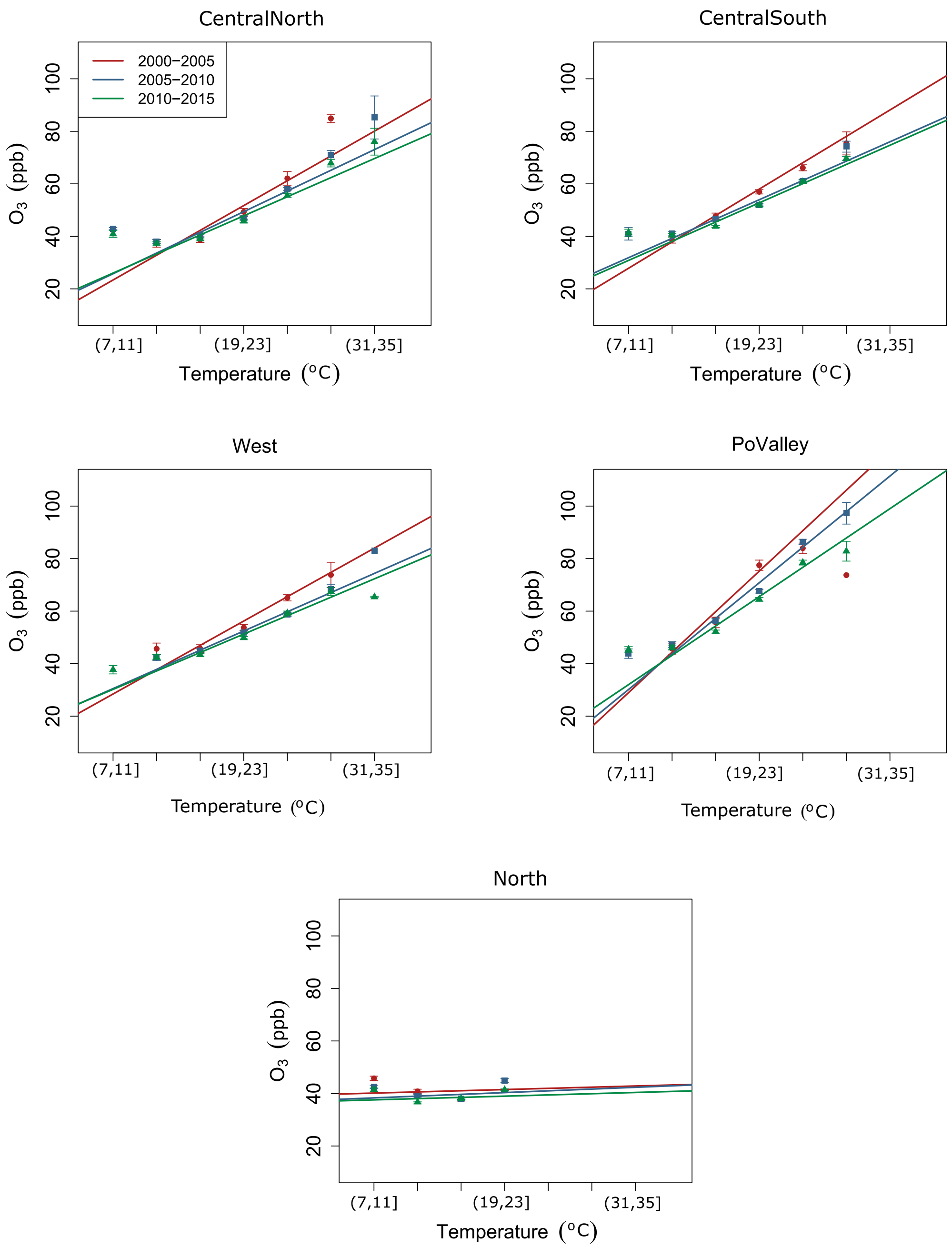

Figure 11. Linear trend of the slope between O_3-temperature daily maximum values for the warm season between May and September. The trends are calculated on the average values for each daily mean S(t) cluster and for the year groups 2000-2005, 2005-2010 and 2010-2015. Points show the mean value for the indicated temperature bin together with the corresponding standard deviation.

year groups. The decrease is consistent for all calculated regional clusters except for "North". For most regions in Europe a significant downward trend of the slope of around 0.04-0.05 ppb/K/year was found (Table 3). At "PoValley" sites the decrease was more pronounced (-0.083 ppb/K/year) . At the same time because of large reductions of precursor concentrations in this region which is characterized by high industrial emissions. Note that the average correlation between O_3 and temperature in that cluster is the highest compared to the other regions, because of large reductions of precursors concentrations in this region which is characterized by high industrial emissions. At the "North" sites the weakest correlation of O_3 to temperature was observed and the trend is non-significant. This is expected because at these high latitudes mean temperature is lower compared to other regions in Europe (Fig. 11), thus, photochemical production of O_3 is weak during the time when O_3 typically reaches its maximum concentration. In addition, in these northern regions the variability of temperature is lower compared to the central and southern parts of Europe, while O_3 concentrations are more influenced by intercontinental transport mechanisms.

In relation to the LT(t)-clusters, it was observed that the higher the pollution burden of the site the stronger the trend of O_3 to temperature slope (Table 4). As shown here, the "HIG" and "MOD" sites have higher trends compared to the clusters "BAC" and "RUR". Our results are in line with a box-model study that tested the O_3–temperature relationship under different NO_x level scenarios (Coates et al., 2016). Coates et al. (2016) have shown that at high NO_x conditions O_3 increases more strongly with temperature, while the increase is less pronounced when moving to lower NO_x conditions. Consequently, regional O_3 production has mainly decreased at the most polluted locations, due to considerable reductions of precursor emissions.

Table 3. Linear trends of the O_3-temperature slope (based on daily maximum values) for the daily mean O_3 S(t)-clusters for the time period 2000-2015. $**$ indicate highly significant trend (p-value$<$ 0.01), $*$ significant (p-value$<$ 0.05) and $-$ indicate non-significant trend (p-value$>$ 0.05).

Daily mean O_3 S(t)-Cluster	**Trend (ppb/K/year)**	**Standard deviation**	**p-value**
CentralNorth	-0.042	0.003	**
CentralSouth	-0.04	0.003	**
West	-0.05	0.004	**
PoValley	-0.083	0.016	**
North	-0.016	0.013	-

Table 4. Linear trends of the O_3-temperature slope (based on daily maximum values) for the daily mean O_3 LT(t)-clusters for the time period 2000-2015. $**$ indicate highly significant trend (p-value$<$ 0.01), $*$ significant (p-value$<$ 0.05) and $-$ indicate non-significant trend (p-value$>$ 0.05).

Daily mean O_3 LT(t)-Cluster	**Trend (ppb/K/year)**	**Standard deviation**	**p-value**
BAC	-0.038	0.006	**
RUR	-0.034	0.006	**
MOD	-0.043	0.003	**
HIG	-0.046	0.003	**

5 Conclusions

In this study, a classification of 291 sites across Europe was performed for the time period 2000-2015. The clustering algorithm applied on the long-term changes LT(t) and the seasonal cycle S(t) of daily mean O_3 resulted in a site type and geographical site classification respectively. Such a ~~classification scheme can be of significant use~~ two-dimensional site classification scheme provides an innovative approach for O_3 trends studies in large spatial domains and can be of significant use in model evaluation studies (e.g. Otero et al., 2018). Our approach captures several features of O_3 variations, i.e. pollution level from the L(t)-clustering and influence of the ~~climatic~~ regional climate conditions from the S(t)-clustering, and presents a unifying perspective on past studies that report different site type labels based on cluster analysis using different metrics of O_3 concentrations. The two-dimensional approach offers a tool beyond traditional clustering studies to study the factors that affect O_3 trends. In addition, O_3 time series analysis is complex and benefits from being characterized in different ways, as well as grouped based on several features. The regional differentiation is hampered by sparse or missing measurement sites in some regions, e.g. eastern Europe or the Balkan peninsula. However, in the last years the number and spatial distribution of sites with longer and more dense measurements has improved.

A trend analysis of de-seasonalized mean O_3 concentrations and meteo-adjusted peak O_3 concentrations was implemented for the considered sites. By using LT(t)- and S(t)-clusters, patterns of O_3 long-term trends across Europe were investigated, based on the multi-dimensional site classification scheme. Long-term trends of de-seasonalized daily mean O_3 are decreasing at the rural sites, while in suburban and urban sites they are either stable or slightly increasing. Positive or flat trends indicate that reduction of precursors has been less effective in reducing O_3 concentrations in heavily polluted environments. On the other hand, downward trends in peak O_3 concentrations were observed in all regions, as a result of precursors emissions reductions. However, peak O_3 has been decreasing with the smallest rate at higher altitude sites especially in the western part of Europe possibly due to the influence of background O_3 imported from North America and East Asia.

The analysis of S(t) extrema revealed a decrease in summertime maxima and an increase in wintertime minima, pointing to a decreasing amplitude of the seasonal cycle of O_3. At the same time the occurrence of the day of maximum has shifted from summer to spring months with a rate of around -0.5 to -1.3 days/year. Changes in the S(t) might be attributed on one hand to the precursors reductions in Europe, and, on the other hand, to changing weather patterns in the northern Atlantic and increase of emissions in southern East Asia.

Finally, the sensitivity of O_3 to temperature has weakened since 2000 with a rate of around ~~0.084~~0.04 ppb/K/year, i.e. formation of O_3 became weaker at high temperature conditions~~due to decreasing~~ , that can be attributed to the decrease of NO_x concentrations. ~~It was shown that differences in changes to this sensitivity across sites are mainly driven by regional~~ The trend of the sensitivity differs across sites that are influenced by different meteorological conditions.

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